

REACTIVE  
DYE  
MIXTURES

Andrea Maria Zamponi

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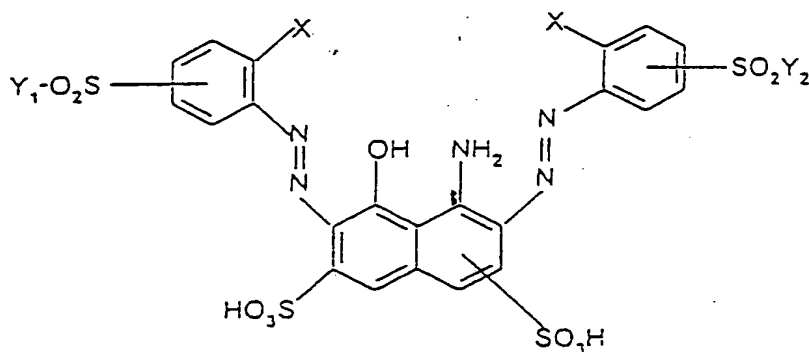
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REACTIVE DYE MIXTURES

This invention relates to mixtures of reactive dyes, in particular to mixtures of reactive dyes containing, as one component, a disazo dye derived from H-acid.

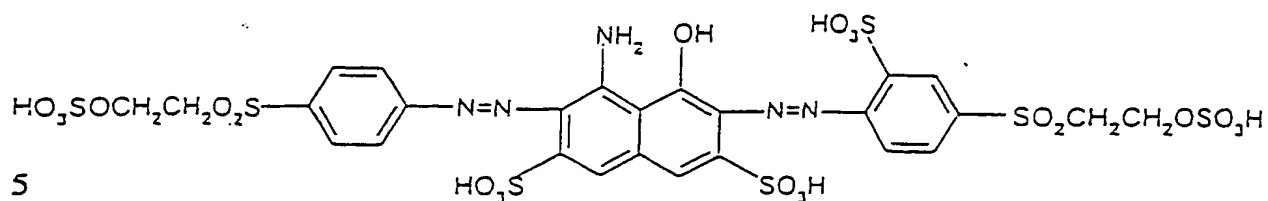
As is well known, reactive dyes contain at least one substituent capable of taking part in a reaction with a group present on a fabric to be dyed during the dyeing operation.

EP-A-0149170 discloses a range of dyes of the formula



in which one X is hydrogen and the other sulpho, each of  $Y_1$  and  $Y_2$  independently is a group  $-\text{CH}=\text{CH}_2$ ,  $-\text{CH}_2\text{CH}_2\text{OSO}_3\text{H}$ ,  $-\text{CH}_2\text{CH}_2\text{SSO}_3\text{H}$ ,  $-\text{CH}_2\text{CH}_2\text{Cl}$  or  $-\text{CH}_2\text{CH}_2\text{OR}$ , and R is a low molecular weight alkanoyl, benzoyl or benzenesulphonyl group, optionally substituted by a  $\text{C}_{1-4}$  alkyl,  $\text{C}_{1-4}$  alkoxy, halogen, carboxy or sulpho group.

A typical dye has the formula



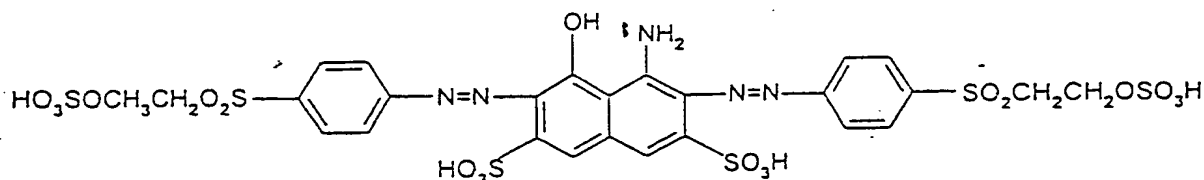
EP-A-0149170 refers only to individual dyes, not mixtures thereof.

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On the other hand, each of EP-A-0224224, EP-A-0679697, EP-A-0531968, EP-A-0668328 and EP-A-0600322 discloses

respective mixtures of dyes, one of which components is a disazo dye derived from H-acid. One particular example of

15 such a dye has the formula



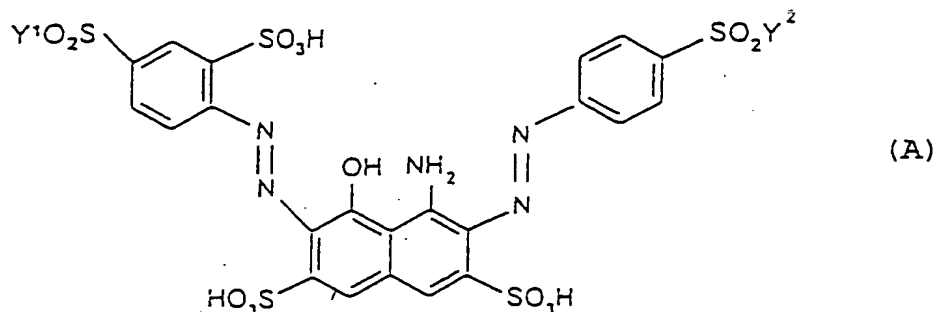
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This dye is available commercially as C.I.Reactive Black 5 and is added to other dyes as a dulling agent where appropriate.

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We find surprisingly that the fastness of a dye mixture can be improved if the dye mixture contains, as a component

thereof, a dye of the formula (A)



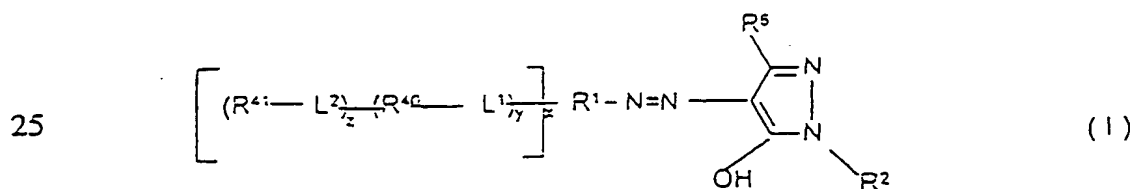
10 wherein each of  $Y^1$  and  $Y^2$ , independently, is a vinyl group or a group of the formula  $-CH_2CH_2Q$  in which  $Q$  is a leaving group removable under alkaline conditions to provide a vinyl group.

15 The dye mixture may contain, in addition to component (A), any of a wide range of dyes.

More particularly, the present invention provides a dye mixture comprising a reactive dye of the formula (A), given and defined above; and

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at least one reactive dye (B) selected from  
(I) a monoazopyrazole dye of the formula



wherein  $R^1$  is an aryl group selected from phenyl and naphthyl groups optionally having at least one substituent thereon, the substituents, or each substituent independently, being selected from a sulphonic acid group and a salt thereof, a  $C_{1-4}$  alkyl group, a  $C_{1-4}$  alkoxy group, a hydroxy group, a carboxyl group, a chlorine atom, a vinyl sulphonyl group and a group  $SO_2CH_2CH_2Q^1$  in which  $Q^1$  is a leaving group removable under alkaline conditions to provide a vinyl sulphonyl group;

10

$R^2$  is a phenyl or naphthyl group, optionally having at least one substituent thereon, the substituent, or each substituent, independently, being selected from a sulphonic acid group and a salt thereof, a  $C_{1-4}$  alkyl group, a  $C_{1-4}$  alkoxy group, a hydroxy group, a chlorine atom, a vinyl sulphonyl group, a group  $SO_2CH_2CH_2Q^2$  in which  $Q^2$  is a leaving group removable under alkaline conditions to provide a vinyl sulphonyl group, a group Het and a group  $L^5$ -Het, where Het is an optionally substituted aromatic heterocyclic reactive or non-reactive group or a reactive or non-reactive group having an aliphatic chain and  $L^5$  is as defined below; and

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$R^6$  is a methyl group, an amide group or a carboxyl group or a salt thereof;

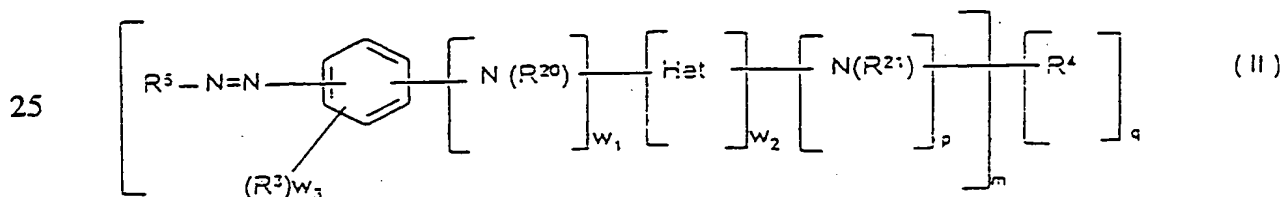
each of  $R^{40}$  and  $R^{41}$ , independently, is an aryl group selected from phenyl and naphthyl groups, each of which, independently, is optionally substituted by a vinylsulphonyl group, a group  $SO_2CH_2CH_2Q^1$  in which  $Q^1$  is a  
 5 leaving group removable under alkaline conditions to provide a vinylsulphonyl group; or the group Het, where Het is as defined above;

at least one of  $R^1$ ,  $R^2$ ,  $R^{40}$  and  $R^{41}$  being, or having thereon  
 10 at least one substituent which is, reactive;

each of  $L^1$ ,  $L^2$  and  $L^5$  independently is a linking group selected from  $N(R^{20})$ , in which  $R^{20}$  is hydrogen or  $C_{1-4}$  alkyl;  $C(=O)$ ;  $C(=O)-O$ ;  $S(=O)_2$ ;  $S(=O)-NH$ ;  $C(=O)-NH$ ; and  $NHC(=O)NH$ ;  
 15 and

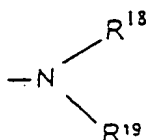
each of  $x$ ,  $y$  and  $z$ , independently, is zero or 1; and, when the group  $R^1$  is substituted by a hydroxy group ortho to the  
 20 azo group, a metallized derivative thereof;

(II) a monoazo or disazo dye of the formula



wherein: Het is an optionally substituted aromatic heterocyclic reactive or non-reactive group or a reactive or non-reactive group having an aliphatic chain;

- 5  $R^3$  or each  $R^3$ , independently, is a chlorine atom, a methyl group, a methoxy group, a sulphonic acid group or a salt thereof, or is an amino group of the formula



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in which each of  $R^{18}$  and  $R^{19}$ , independently, is hydrogen, chloro, methyl, ( $C_{1-4}$  alkyl) carbonyl, aminocarbonyl, vinylsulphonyl or a group  $SO_2CH_2CH_2Q^1$ , in which  $Q^1$  is as defined above;

15

- $R^4$ , or each  $R^4$  independently, is hydrogen, a sulphonic acid group or a salt thereof, a  $C_{1-8}$  alkyl (preferably a  $C_{1-4}$  alkyl) group, a  $C_{1-4}$  alkoxy group, a vinyl sulphonyl group or a group  $SO_2CH_2CH_2Q^2$  in which  $Q^2$  is a
- 20 leaving group removable under alkaline conditions to provide a vinyl sulphonyl group, which  $C_{1-4}$  alkyl group or  $C_{1-4}$  alkyl moiety of the  $C_{1-4}$  alkoxy group is optionally interrupted by an oxygen atom to provide an ether group and is optionally substituted by a vinyl sulphonyl group or a
- 25 group  $SO_2CH_2CH_2Q^2$ , in which  $Q^2$  is as defined above; or  $R^4$  (or when  $q$  is 2, each  $R^4$  independently) is a phenyl group optionally substituted by at least one sulphonic acid group

or a salt thereof or at least one group Het, where Het is as defined above; or  $R^4$  is a group Het, where Het is as defined above

5  $R^5$  is an aryl group selected from phenyl and naphthyl groups each optionally substituted by at least one sulphonic acid group or, a salt thereof or at least one group Het, as defined above;

$R^{20}$  is a hydrogen atom or a  $C_{1-4}$  alkyl group;

10  $R^{21}$  is a hydrogen atom, a  $C_{1-4}$  alkyl group, a sulphonic acid- $C_{1-4}$  alkyl group, a chloroalkylsulphonyl- $C_{1-4}$  alkyl group or a group Het, where Het is as defined above;

$m$  is 1 or 2;

$p$  is zero, 1 or 2;

15  $q$  is zero, 1 or 2;

each of  $w_1$  and  $w_2$  is zero or 1; and

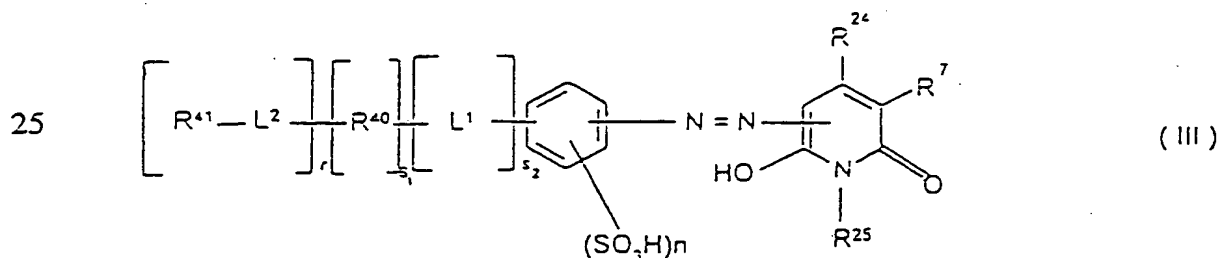
$w_3$  is 1, 2 or 3; and

when  $p$  is zero,  $q$  is zero;

at least one of  $R^4$ ,  $R^5$ ,  $R^{18}$ ,  $R^{19}$ ,  $R^{21}$  and Het being,

20 or having thereon at least one substituent which is, reactive;

(III) a monoazopyridone dye of the formula





wherein: each of  $R^{40}$ ,  $R^{41}$ ,  $L^1$  and  $L^2$  is as defined above;

$R^7$  is optionally present and is a cyano group or the group  $-CH_2SO_3H$  or the group  $-C(=O)NH_2$ ;

each of  $R^{24}$  and  $R^{25}$ , independently, is a hydrogen atom, a  $C_{1-4}$  alkyl group, a sulpho- $C_{1-4}$  alkyl group, or a carboxyl group;

$n$  is 1 or 2;

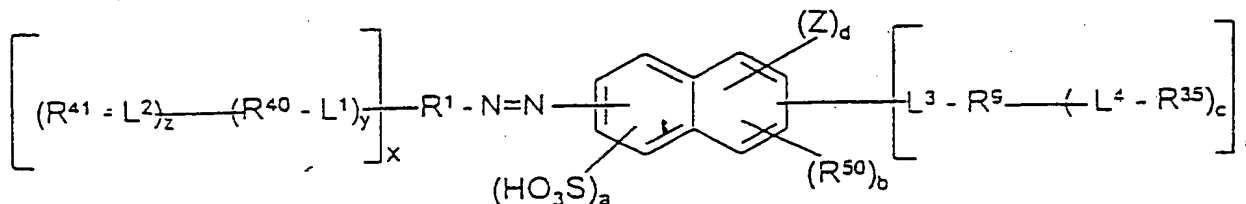
$r$  is zero or 1; and

each of  $s_1$  and  $s_2$  is zero or 1; and when  $R^{40}$  is a phenyl or naphthyl group  $s_2$  is 1;

at least one of  $R^{40}$  and  $R^{41}$  being, or having thereon at least one substituent which is, reactive;

(IV) a monoazonaphthyl dye of the formula

15



(IV)

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wherein: each of  $R^1$ ,  $R^{40}$ ,  $R^{41}$ ,  $L^1$ ,  $L^2$ ,  $x$ ,  $y$  and  $z$  is as defined above;

$R^9$  is  $CH_3(C=O)-$ , Het (as defined above) or an aryl group selected from phenyl and naphthyl, which Het or aryl group is optionally substituted by at least one substituent, the or each substituent, independently, being

selected from a sulphonic acid group and a salt thereof, a C<sub>1-4</sub> alkyl group, a C<sub>1-4</sub> alkoxy group, a hydroxy group, an amino group optionally substituted by at least one methyl or sulphato group, a vinyl sulphonyl group and a group

5 SO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Q<sup>1</sup> in which Q<sup>1</sup> is as defined above;

R<sup>35</sup> is a C<sub>1-4</sub> alkyl or C<sub>2-4</sub> alkenyl group, which C<sub>1-4</sub> alkyl or C<sub>2-4</sub> alkenyl group is optionally substituted by at least one halogen atom, a sulphonic acid group or salt

10 thereof, a chloroalkylsulphonyl group, a vinylsulphonyl group or -SO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Q<sup>1</sup>, where Q<sup>1</sup> is as defined above and which C<sub>1-4</sub> alkyl or C<sub>2-4</sub> alkenyl group optionally additionally contains at least one oxygen or sulphur atom in the chain thereof; the group Het (as defined above); or an aryl group

15 selected from phenyl and naphthyl, which Het or aryl group is optionally substituted by at least one substituent, the substituent or each substituent independently, being selected from a sulphonic acid group and a salt thereof, a C<sub>1-4</sub> alkyl group, a C<sub>1-4</sub> alkoxy group, a halogen atom, a

20 hydroxy group, an amino group optionally substituted by at least one methyl or sulphato group, a vinylsulphonyl group, a vinylsulphonyloxyethyl group and a group SO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Q<sup>1</sup> in which Q<sup>1</sup> is as defined above;

25 R<sup>50</sup> is a vinylsulphonyl group or a group SO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Q<sup>1</sup> (in which Q<sup>1</sup> is as defined above);

at least one of R<sup>1</sup>, R<sup>9</sup>, R<sup>35</sup>, R<sup>40</sup>, R<sup>41</sup> and R<sup>50</sup> is, or

has thereon at least one substituent which is, reactive;

$L^3$  is a linking group selected from  $N(R^{20})$ , in which  $R^{20}$  is as defined above; CO; COO; NHCO; NHCONH;  $SO_2NH$  and  $SO_2$ ;

$L^4$  is a linking group selected from  $N(R^{21})$ , in which  $R^{21}$  is as defined above, CO, COO, NHCO, NHCONH,  $SO_2NH$  and  $SO_2$ ;

Z is hydroxy, amino or methylamino;

a is zero or 1-4;

b is zero or 1-3;

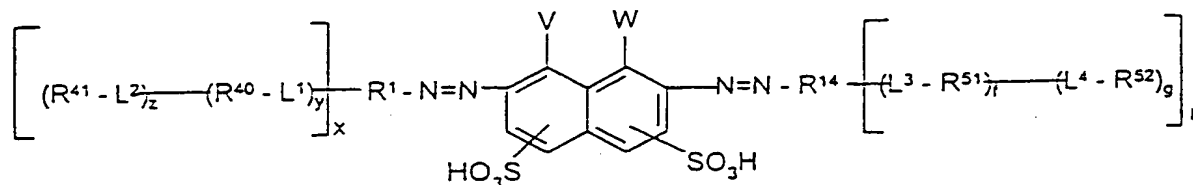
c is zero or 1;

d is zero, 1 or 2;

e is zero or 1; and

when each of  $R^1$  and Z provides a hydroxyl group ortho to the azo group, a metallized derivative thereof;

(V) a disazoaminonaphthyl dye of the formula

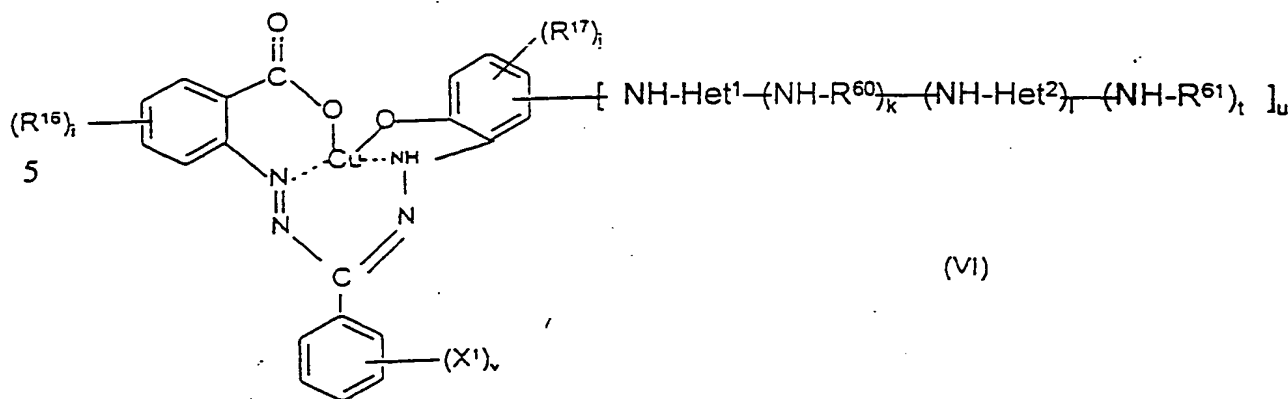


(V)

wherein: each of  $R^1$ ,  $R^{40}$ ,  $R^{41}$ ,  $L^1$ ,  $L^2$ , x, y and z is as defined above;



(VI) a formazan dye of the formula.



wherein: each of  $R^{16}$  and  $R^{17}$  independently of one another, each  $R^{16}$  independently of one another and each  $R^{17}$  independently of one another, is a sulphonic acid group or a salt thereof, a vinyl sulphonyl group or a group  $SO_2CH_2CH_2Q^1$  in which  $Q^1$  is a leaving group removable under alkaline conditions to provide a vinyl sulphonyl group;

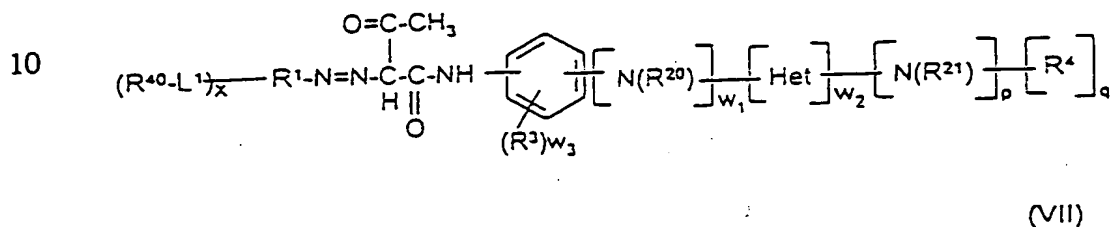
each of  $Het^1$  and  $Het^2$ , independently, is an optionally substituted aromatic heterocyclic reactive or non-reactive group or a reactive or non-reactive group having an aliphatic chain; and

each of  $R^{60}$  and  $R^{61}$ , independently, is an aryl group selected from phenyl and naphthyl groups each of which is optionally substituted by a sulphonic acid group or a salt thereof, a vinylsulphonyl group or a group  $SO_2CH_2CH_2Q^1$  in which  $Q^1$  is as defined above;

$X^1$  is a sulphonic acid group or a salt thereof or halogen; each of  $i$ ,  $j$  and  $v$ , independently, is zero, 1 or 2; and each of  $k$ ,  $l$ ,  $t$  and  $u$ , independently, is zero or 1; and

at least one of  $R^{16}$ ,  $R^{17}$ ,  $R^{50}$ ,  $R^{51}$ ,  $Het^1$  and  $Het^2$  is, or has thereon at least one substituent which is, reactive;

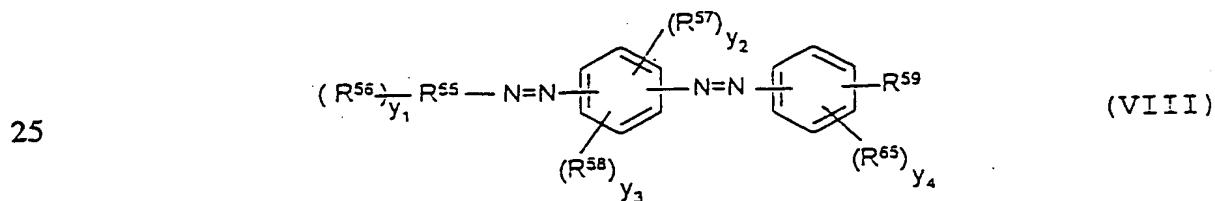
(VII) a dye of the formula



wherein: each of  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^{20}$ ,  $R^{21}$ ,  $R^{40}$ ,  $L^1$ ,  $Het$ ,  $x$ ,  $p$ ,  $q$ ,  $w_1$ ,  $w_2$  and  $w_3$  is as defined above; and

at least one of  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^{21}$ ,  $R^{40}$  and  $Het$  is, or has thereon, at least one substituent which is, reactive;

(VIII) a disazo dye of the formula



wherein R<sup>55</sup> is an aryl group selected from phenyl and naphthyl groups;

$R^{56}$  is a sulphonic acid group or a salt thereof or a reactive group selected from a vinyl sulphonyl group and a group  $SO_2CH_2CH_2Q^1$  in which  $Q^1$  is a leaving group removable under alkaline conditions to provide a vinyl sulphonyl group;

$R^{57}$  is an amino group or a group  $NHR^A$  in which  $R^A$  is a  $C_{1-4}$  alkyl group;

10 R<sup>58</sup> is a sulphonic acid group or a salt thereof;

R<sup>59</sup> is a sulphonic acid group or a salt thereof, a reactive group selected from a vinyl sulphonyl group and a group SO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Q<sup>2</sup> in which Q<sup>2</sup> is a leaving group removable under alkaline conditions to provide a vinyl sulphonyl group; or the group R<sup>59</sup> is a group Het or a group L<sup>10</sup>-Het, where Het is an optionally substituted aromatic heterocyclic reactive or non-reactive group;

$R^{65}$  is a ureido group or a group  $HNC(=O)R^B$  in which  $R^B$  is a  $C_{1-4}$  alkyl group;

20  $L^{10}$  is a linking group selected from  $N(R^{20})$ , in which  $R^{20}$  is hydrogen or  $C_{1-4}$  alkyl;  $C(=O)$ ;  $C(=O)-O$ ;  $S(=O)_2$ ;  $S(=O)-NH$ ;  $C(=O)-NH$ ; and  $NHC(=O)NH$ ;

$y_1$  is zero, 1, 2 or 3;

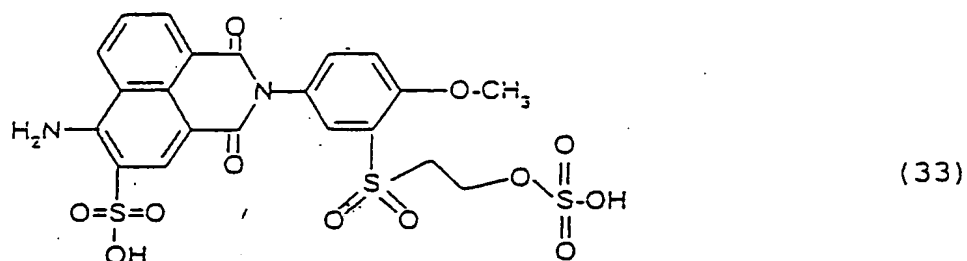
$y_2$  is zero, 1 or 2;

25  $y_3$  is zero or 1; and

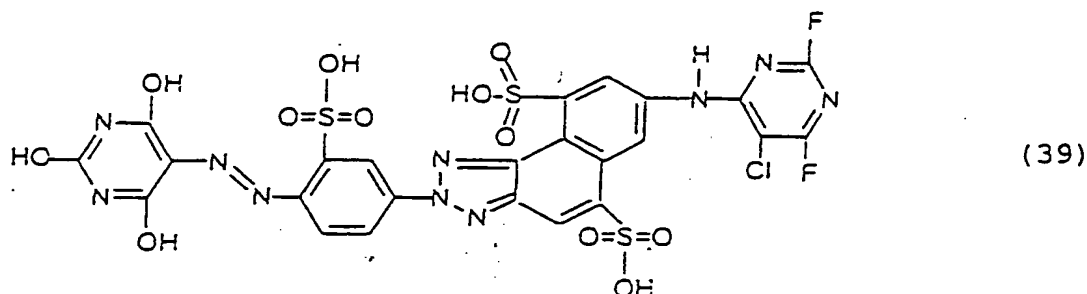
$y_4$  is zero or 1; and

at least one of  $R^{56}$  and  $R^{59}$  is a reactive group.

(IX) a dye of the formula



or



(X) a metal phthalocyanine dye of the formula



wherein: MPC is a metallophthalocyanine chromophore;

each of  $\text{R}^{70}$  and  $\text{R}^{71}$ , independently, is hydrogen or

$\text{C}_{1-4}$  alkyl;

B is a hydrocarbon bridging group;



Het is a reactive heterocyclic group;

each of  $x_1$ ,  $x_2$  and  $x_3$  is a respective average value;

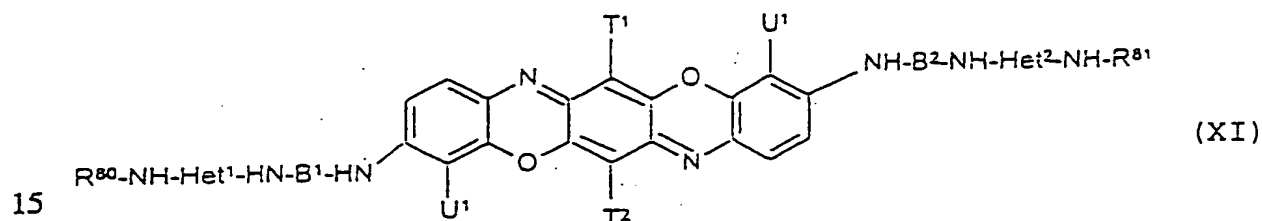
$$x_1 + x_2 + x_3 = 4;$$

5  $x_1$  is at least 1

$x_2$  is zero or 1; and

$x_3$  is at least 1; and

(XI) a triphenodioxazine dye of the formula (XI) (or a salt thereof)



wherein: each of  $B^1$  and  $B^2$ , independently, is a hydrocarbon bridging group;

20  $U^1$  is H or  $SO_3H$ ; and

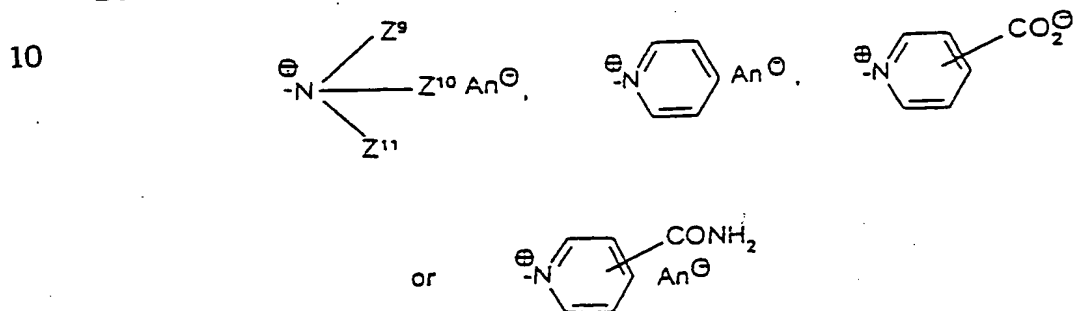
each of  $T^1$  and  $T^2$ , independently, is halo,  $C_{1-4}$  alkyl, or  $C_{1-4}$  alkoxy;

25 each of  $R^{80}$  and  $R^{81}$  is a phenyl group substituted by at least one sulphonic acid group or a salt thereof;

each of  $Het^1$  and  $Het^2$  is as defined above; and

at least one of Het<sup>1</sup> and Het<sup>2</sup> is a reactive group.

Referring to the dye of the formula (A), preferably at least one of Y<sup>1</sup> and Y<sup>2</sup> is the group -CH<sub>2</sub>CH<sub>2</sub>Q and Q is selected from chlorine, bromine, C<sub>1-4</sub>-alkylsulfonyl, phenylsulfonyl, OSO<sub>3</sub>H, SSO<sub>3</sub>H, OP(O)(OH)<sub>2</sub>, C<sub>1-4</sub>-alkylsulfonyloxy, phenylsulfonyloxy, (C<sub>1-4</sub> alkyl) carbonyloxy, (C<sub>1-4</sub> dialkyl) amino or a radical of the formula



15 where Z<sup>9</sup>, Z<sup>10</sup> and Z<sup>11</sup> are identical or different and are each, independently of one another, C<sub>1-4</sub> alkyl or benzyl and An<sup>⊖</sup> is in each case one equivalent of an anion. More preferably, each of Y<sup>1</sup> and Y<sup>2</sup> is the group HO<sub>3</sub>SOCH<sub>2</sub>CH<sub>2</sub>.

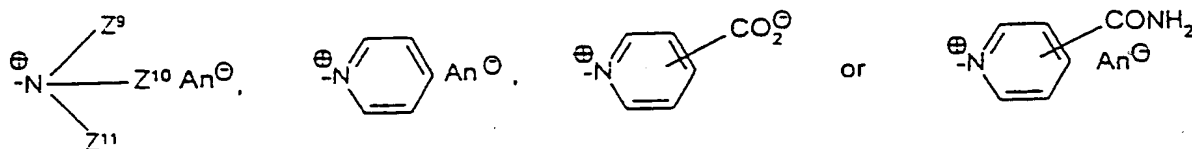
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Referring now to the reactive dye (B), dyes in one preferred range thereof contain a group Het, where Het is an optionally substituted aromatic heterocyclic reactive group derived from a halogen-substituted heterocyclic compound selected from 1,3,5-triazine, quinoxaline, phthalazine, pyrimidine, pyridazine and 2-(C<sub>1-4</sub> alkylsulphonyl) benzothiazole. More preferably, the aromatic heterocyclic reactive group is substituted and at

least one substituent is a halogen atom.

An alternative preferred range of reactive dyes (B) contains a group Het, where Het is a reactive group having an aliphatic chain and selected from acryloyl, mono-, di- or trichloroacryloyl, mono-, di- or tri- bromoacryloyl, -CO-CCl=CH-COOH, -CO-CH=CCl-COOH, 2-chloropropionyl, 1,2-dichloropropionyl, 1,2-dibromopropionyl, 3-phenylsulfonylpropionyl, 3-methylsulfonylpropionyl, 2-sulfatoethylaminosulfonyl, 2-chloro-2,3,3-trifluorocyclobutylcarbonyl, 2,2,3,3-tetrafluorocyclobutylcarbonyl, 2,2,3,3-tetrafluorocyclobutylsulfonyl, 2-(2,2,3,3-tetrafluorocyclobutyl)acryloyl, 1- or 2-alkyl- or 1- or 2-arylsulfonylacryloyl, or a radical of the formula SO<sub>2</sub>-Y<sup>3</sup>, SO<sub>2</sub>NH-Y<sup>3</sup>, CONH-L<sup>6</sup>-SO<sub>2</sub>-Y<sup>3</sup>, or NHCONH-L<sup>6</sup>-SO<sub>2</sub>-Y<sup>3</sup> where L<sup>6</sup> is C<sub>1</sub>-C<sub>4</sub>-alkylene or phenylene and Y<sup>3</sup> is a vinyl group or a group of the formula CH<sub>2</sub>CH<sub>2</sub>Q<sup>3</sup> in which Q<sup>3</sup> is a leaving group removable under alkaline conditions to provide a vinyl group.

It is also preferred that, the reactive dye (B) has at least one of the groups Q<sup>1</sup> and Q<sup>2</sup> therein and the or each of groups Q<sup>1</sup> and Q<sup>2</sup> independently is selected from chlorine, bromine, C<sub>1-4</sub>-alkylsulfonyl, phenylsulfonyl, OSO<sub>3</sub>H, SSO<sub>3</sub>H, OP(O)(OH)<sub>2</sub>, C<sub>1-4</sub>-alkylsulfonyloxy, phenylsulfonyloxy, (C<sub>1-4</sub> alkyl) carboxyloxy, (C<sub>1-4</sub> dialkyl) amino or a radical of the formula



where  $Z^9$ ,  $Z^{10}$  and  $Z^{11}$  are identical or different and are each, independently of one another,  $C_{1-4}$ -alkyl or benzyl and  $An^e$  is in each case one equivalent of an anion.

5

In a dye mixture wherein the reactive dye (B) is a monoazopyrazole dye of the formula (I), given and defined above, it is preferred that at least one of the group

10  $[(R^{41}-L^2)_z(R^{40}-L^1)_y]_xR^1$  and the group  $R^2$  has at least one sulphonic acid group substituted thereon and at least the other of the group  $[(R^{41}-L^2)_z(R^{40}-L^1)_y]_xR^1$  and the group  $R^2$  has a group  $-SO_2CH_2SO_2Q^2$  substituted thereon,  $Q^2$  being as defined above.

15 In respective preferred ranges of the reactive dye (B) of the formula (I)

(i)  $x'$  is zero and the group  $R^1$  is substituted by at least one of a sulphonic acid group and the group  
20  $-SO_2CH_2SO_2Q^1$ , wherein  $Q^1$  is as defined above;

(ii) each of  $x$ ,  $y$  and  $z$  is 1, each of  $L^1$  and  $L^2$  is NH,  $R^{40}$  is the group Het, where Het is a triazine ring substituted by a halogen atom and  $R^{41}$  is an optionally  
25 substituted phenyl group.

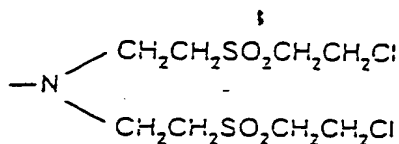
(iii) each of  $x$  and  $z$  is 1,  $y$  is zero,  $L^2$  is NH and  $R^{41}$  is the group Het, where Het is a difluorochloropyrimidinyl

group; and

- (iv) each of x and z is 1, y is zero, L<sup>2</sup> is CONH (in which the nitrogen atom is attached to the group R<sup>1</sup> and the carbon to the group R<sup>41</sup>) and R<sup>41</sup> is the group Het, where Het is a 2,3-dichloroquinoxaline group.

In a reactive dye (B) of the formula (I), R<sup>2</sup> is preferably a phenyl or naphthyl group substituted by

- (i) at least one of a sulphonic acid group and the group -SO<sub>2</sub>CH<sub>2</sub>SO<sub>2</sub>Q<sup>2</sup>, where Q<sup>2</sup> is as defined in claim 1; or
- (ii) at least by the group NH-Het, where Het is a triazine ring substituted by a halogen atom and optionally substituted by the group



In a reactive dye (B) of the formula (I), the group R<sup>1</sup> may be substituted by a hydroxy group ortho to the azo group and the reactive dye (B) may then be in the form of a copper complex.

Reference is now made to a dye mixture wherein the reactive dye (B) is monoazo or disazo dye of the formula (II), given

and defined above.

In such a mixture it is preferred that in the reactive dye (B) of the formula (II), when  $m$  is 1 and  $R^4$  is alkyl,  $R^4$  is C<sub>1-4</sub> alkyl.

It is also preferred that the group  $R^5$  is an aryl group selected from phenyl and naphthyl groups each substituted by at least one sulphonic acid group or a salt thereof or by a group Het, wherein Het is a vinylsulphonyl group or a group  $SO_2CH_2CH_2Q^1$  in which  $Q^1$  is as defined above.

In an especially preferred reactive dye (B) of the formula (II),  $m$  is 1, so that the dye is a monoazo dye.

In preferred ranges of monoazo dyes (B) of the formula (II) in a mixture in accordance with the invention,

(i) each of  $w_1$ ,  $w_2$ ,  $p$  and  $q$  is zero,  $w_3$  is at least 2, at least one of the groups  $R^3$  is a sulphonic acid group and the group  $R^5$  is an aryl group selected from phenyl and naphthyl groups each substituted by a vinylsulphonyl group or a group  $-SO_2CH_2CH_2Q^1$ , where  $Q^1$  is as defined above.

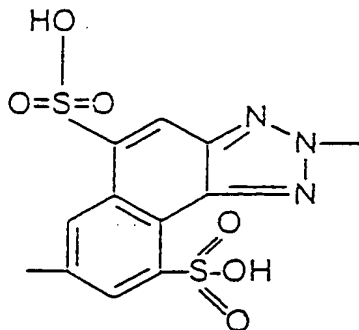
(ii) each of  $w_1$  and  $w_2$  is zero, each of  $p$  and  $q$  is 1,  $R^{21}$  is hydrogen and  $R^4$  is selected from a triazine ring substituted by at least one halogen atom and optionally additionally substituted by an amino group; and a pyrimidine group substituted by at least one halogen atom and optionally additionally substituted by a methyl group;

(iii) each of  $w_1$ ,  $w_2$ ,  $p$  and  $q$  is 1,  $R^{20}$  is hydrogen, Het

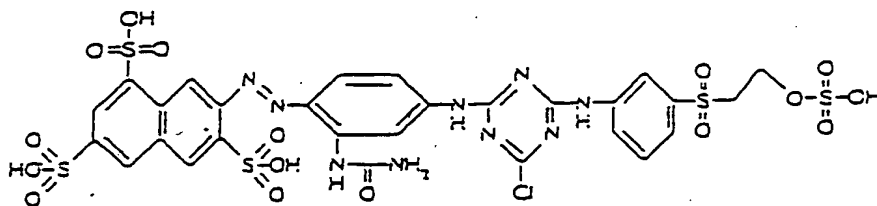
is a triazine ring substituted by a halogen atom,  $R^{21}$  is hydrogen and  $R^4$  is selected from a phenyl group or a group  $-\text{SO}_2\text{CH}_2\text{CH}_2\text{Q}^1$ , where  $\text{Q}^1$  is as defined above, and a straight or branched  $\text{C}_{2-4}$  alkylene chain substituted by a substituent  
 5 selected from a hydroxyl group; a sulphonic acid group or salt thereof; a vinylsulphonyl group, a group  $-\text{SO}_2\text{CH}_2\text{CH}_2\text{Q}^2$ , where  $\text{Q}^2$  is as defined above; and a pyrimidinylamino group in which the pyrimidinyl group is substituted by at least one halogen atom and optionally additionally by a methyl  
 10 group; and which straight or branched  $\text{C}_{2-4}$  alkylene group optionally contains a hetero atom selected from O, S and N(H);

(iv) each of  $w_1$  and  $w_2$  is zero, each of p and q is 1  
 15 and each of  $R^{21}$  and  $R^4$  is the group  $\text{OSO}_3\text{H}$ ; and

(v)  $w_1$  is zero,  $w_2$  is 1, p is 1, q is 1,  $R^{21}$  is hydrogen,  $R^4$  is a pyrimidinyl group substituted by at least one halogen atom and optionally additionally substituted by  
 20 a methyl group and Het is a non-reactive heterocyclic group of the formula



An especially preferred dye mixture contains a dye of the formula (44) as the reactive dye (B) of formula (II)



Reference is now made to a dye mixture wherein the reactive dye (B) is a monoazopyridone dye of the formula (III), given and defined above.

In respective preferred ranges of the reactive dye (B) of the formula (III),

(i) each of  $r$ ,  $s_1$  and  $s_2$  is 1, each of  $L^1$  and  $L^2$  is NH,  $R^{40}$  is a triazine ring substituted by a halogen atom and  $R^{41}$  is selected from a phenyl group substituted by at least one of a chlorine atom, a sulphonic acid group or a salt thereof, a vinylsulphonyl group or a group  $-SO_2CH_2CH_2Q^1$ , where  $Q^1$  is as defined above; and a straight or branched chain  $C_{2-4}$  alkylene group optionally containing at least one oxygen atom and substituted by a vinylsulphonyl group or a group  $-SO_2CH_2CH_2Q^1$ , where  $Q^1$  is as defined above;

(ii) each of  $r$  and  $s_1$  is 1,  $s_2$  is zero,  $L^2$  is NH,  $R^{41}$  is



a pyrimidinyl group substituted by at least one halogen atom and optionally additionally substituted by a methyl group and  $R^{40}$  is a naphtho-(1,2-d)-1,2,3-triazole substituted by at least one sulphonic acid group or salt thereof; and

(iii) each of  $r_1$ ,  $s_1$  and  $s_2$  is 1,  $L^1$  is CONH (in which the carbon atom is attached to the group  $R^{40}$ ),  $L^2$  is NH,  $R^{40}$  is an optionally substituted phenyl group and  $R^{41}$  is a pyrimidinyl group substituted by at least one halogen atom and optionally additionally substituted by a methyl group.

Reference is now made to a dye mixture wherein the reactive dye (B) is a monoazonaphthyl dye of the formula (IV), given and defined above.

In one preferred range of such dyes,

(i)  $x$  is zero,  $d$  is 1 and  $a$  or  $b$  is 1. More preferably  $e$  is zero.

In other preferred respective ranges,

(ii)  $x$  is 1,  $y$  is zero,  $z$  is 1,  $L^2$  is NH and  $R^{41}$  is a pyrimidinyl group substituted by at least one halogen atom and optionally additionally substituted by a methyl group;

(iii)  $x$  is 1,  $y$  is zero,  $z$  is 1,  $L^2$  is CONH (with the

carbon atom attached to the group  $R^1$  and the nitrogen atom to the group  $R^{41}$ ) and  $R^{41}$  is a phenyl group substituted by a vinylsulphonyl group or a group  $-SO_2CH_2CH_2Q^1$ , where  $Q^1$  is as defined above; and

5

(iv) each of  $x$ ,  $y$  and  $z$  is 1, each of  $L^1$  and  $L^2$  is NH,  $R^{40}$  is a triazine ring substituted by a halogen atom and  $R^{41}$  is an aromatic group selected from phenyl and naphthyl groups each substituted by at least one of a sulphonic acid group or a salt thereof, a vinylsulphonyl group and the group  $-SO_2CH_2CH_2Q^1$ , where  $Q^1$  is as defined above.

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In such ranges (ii) - (iv) of dyes (B) of the formula (IV), more preferably,  $e$  is zero.

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In other preferred ranges of the reactive dye (B) of the formula (IV),

(v)  $e$  is 1,  $c$  is zero,  $L^3$  is CONH (where either the nitrogen or carbon atom thereof is attached to the group  $R^9$ ) and  $R^9$  is a methyl group;

20

(vi)  $e$  is 1,  $c$  is zero,  $L^3$  is CONH (where either the nitrogen or carbon atom thereof is attached to the group  $R^9$ ) and  $R^9$  is a phenyl group optionally substituted by at least one substituent, the or each substituent being selected from methoxy, carboxyethyl, sulphoethyl, carboxyethenyl, 1,2-dibromoalkyl, chloroethylsulphonyl, vinylsulphonyl, a

25

group of the formula  $-\text{SO}_2\text{CH}_2\text{CH}_2\text{Q}^1$ , where  $\text{Q}^1$  is as defined above and a 2,3-dichloroquinoxaline group.

(vii) e is 1, c is 1,  $\text{L}^3$  is CONH (where either the nitrogen or carbon atom thereof is attached to the group  $\text{R}^9$ ),  $\text{R}^9$  is a phenyl group substituted at least by the group  $\text{L}^4\text{-R}^{35}$ , where  $\text{L}^4$  is NH and  $\text{R}^{35}$  is a vinyl group optionally substituted by a halogen atom or a pyrimidinyl group substituted by a halogen atom and optionally additionally substituted by a methyl group; and

(viii) e is 1, c is zero,  $\text{L}^3$  is  $\text{N}(\text{R}^{20})$ , where  $\text{R}^{20}$  is as defined above (and is more preferably a hydrogen atom or a methyl group) and  $\text{R}^9$  is a vinylsulphonyl group, a group  $-\text{SO}_2\text{CH}_2\text{CH}_2\text{Q}^1$  wherein  $\text{Q}^1$  is as defined in claim 1, or a pyrimidinyl group substituted by a halogen atom and optionally additionally substituted by a methyl group.  
In yet another preferred range

(ix) e is 1, c is zero,  $\text{L}^3$  is  $\text{N}(\text{R}^{20})$ , where  $\text{R}^{20}$  is as defined above and  $\text{R}^9$  is a triazine ring substituted by at least one halogen atom. In this range the triazine ring is preferably substituted by two halogen atoms or by one halogen atom and a morpholinyl group.

In another preferred range,

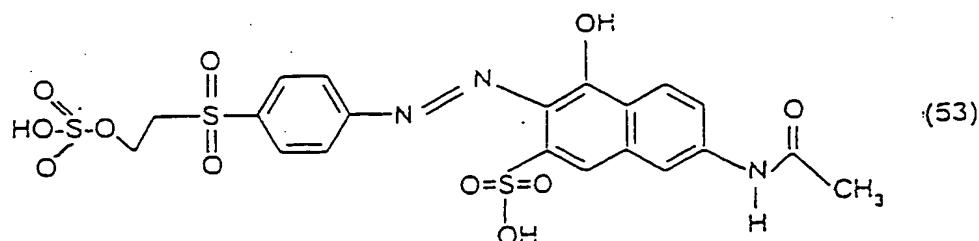
(x) e is 1, c is 1,  $\text{L}^3$  is  $\text{N}(\text{R}^{20})$ , where  $\text{R}^{20}$  is as

defined above,  $L^4$  is the group  $R^{21}$ , where  $R^{21}$  is as defined above, and  $R^{35}$  is selected from a phenyl group optionally substituted by a sulphonic acid group or salt thereof, a halogen atom, a vinylsulphonyloxyalkyl group, a vinylsulphonyl group or the group  $-SO_2CH_2CH_2Q^1$ , where  $Q^1$  is as defined above; and a  $C_{1-4}$  alkyl group optionally substituted by a vinylsulphonyl group, the group  $-SO_2CH_2CH_2Q^1$ , where  $Q^1$  is as defined above, a sulphonic acid group or a salt thereof or a chloroalkylsulphonyl group, which  $C_{1-4}$  alkyl group optionally additionally contains at least one oxygen or sulphur atom in the chain thereof.

In dye mixtures containing a reactive dye (B) of the formula (IV) within the above ranges  $x$  is preferably zero.

In the reactive dye (B) of the formula (IV), each of the groups  $R^1$  and the naphthalene nucleus may be substituted by a respective hydroxyl group ortho to the azo group and the reactive dye (B) may then be in the form of a copper complex thereof.

An especially preferred dye mixture contains a dye of the formula (53) as the reactive dye (B)



Reference is now made to a dye mixture wherein the reactive dye (B) is a disazo dye of the formula (V), given and defined above. In such dyes, the respective sulphonic acid groups on the naphthalene nucleus are preferably in the 3- and 6- positions (i.e. such dyes are preferably derived from H-acid).

In one preferred range of dyes of the formula

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(i) V is amino, W is hydroxy, each of  $R^1$  and  $R^{1'}$  is a phenyl group substituted by at least one substituent, the or each substituent independently being selected from a sulphonic acid group or a salt thereof, a vinyl sulphonyl group and a group  $SO_2CH_2CH_2Q^1$ , where  $Q^1$  is as defined above and  $R^{1'}$  is optionally additionally substituted by at least one methoxy group.

It is also preferred, especially for one sub-range within the range (i), that each of x and h is zero. Such a range of dyes includes those of the formula (A) and a mixture in accordance with the invention may indeed contain only dyes of the formula (A), one such dye of the mixture being regarded as a dye of the formula (A) and at least one other such dye of the mixture being regarded as a dye of the formula (V).

In an alternative preferred range of dyes of the formula

(V), especially for another sub-range within the range (i), at least one of x and h is 1 and more preferably each of x and h is 1.

- 5 In a preferred sub-range (ii) of dyes (B) of the formula (V), within the range (i), x, y and z is 1, each of  $L^1$  and  $L^2$  is NH,  $R^{40}$  is a triazine ring substituted by a halogen atom and  $R^{41}$  is a phenyl group substituted by at least one substituent, the or each substituent independently being  
10 selected from a sulphonic acid group or a salt thereof, a vinylsulphonyl group and a group  $SO_2CH_2CH_2Q^1$ , where  $Q^1$  is as defined above.

- In the preferred ranges (i) and (ii) above, more  
15 preferably, each of f, g and h is 1, each of  $L^3$  and  $L^4$  is NH,  $R^{51}$  is a triazine ring substituted by a halogen atom and  $R^{52}$  is a phenyl group substituted by at least one substituent, the or each substituent independently being  
selected from a halogen atom, a sulphonic acid group or a  
20 salt thereof, a vinylsulphonyl group and a group  $SO_2CH_2CH_2Q^1$ , where  $Q^1$  is as defined above.

- In a preferred range (iii) of reactive dyes (B) of the formula (V), V is amino, W is hydroxy, h is zero and  $R^{14}$  is  
25 a naphthalene group substituted by at least one sulphonic acid group. More preferably, in this range (iii), each of x, y and z is 1,  $R^1$  is a phenyl group optionally substituted by a sulphonic acid group or a salt thereof, each of  $L^1$  and

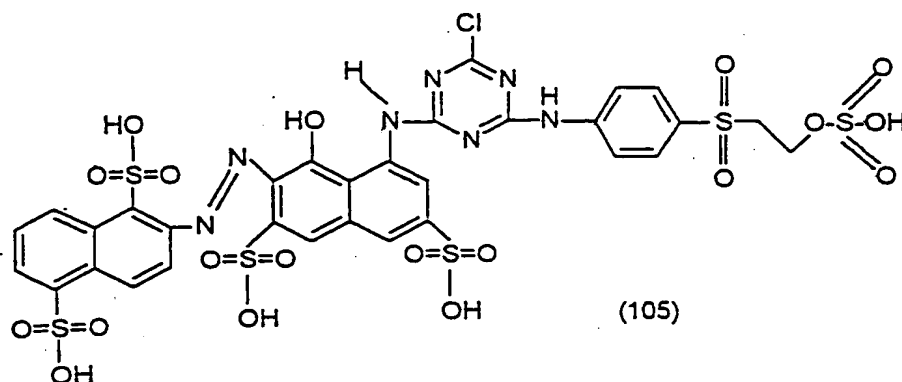
$L^2$  is NH,  $R^{40}$  is a triazine ring substituted by a halogen atom and  $R^{41}$  is a phenyl group substituted by at least one substituent, the or each substituent independently being selected from a sulphonic acid group or a salt thereof, a vinylsulphonyl group and a group  $SO_2CH_2CH_2Q^1$ , where  $Q^1$  is as defined above.

In a preferred range (iv) of the reactive dyes (B) of the formula (V), V is amino, W is hydroxy, h is 1, f is zero, g is 1,  $L^4$  is NH and  $R^{52}$  is the group Het<sup>3</sup>, where Het<sup>3</sup> is a substituted aromatic heterocyclic group. In this range (iv), more preferably the group Het<sup>3</sup> is a pyrimidinyl group substituted by at least one halogen atom and optionally additionally substituted by a methyl group and still more preferably x is zero and  $R^1$  is a phenyl group substituted by a vinylsulphonyl group or  $SO_2CH_2CH_2Q^1$ , where  $Q^1$  is as defined above.

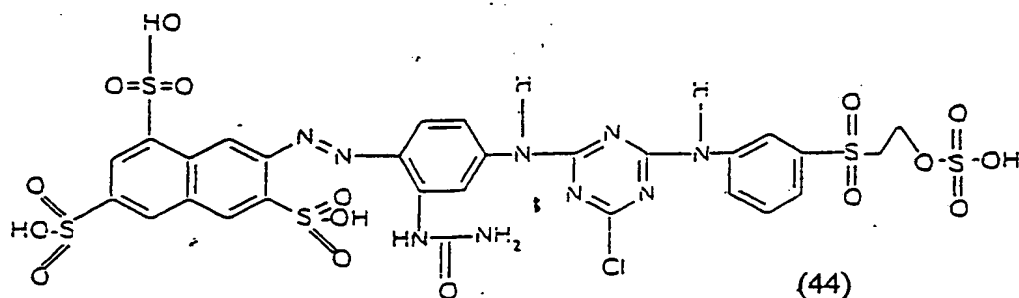
In a preferred range (v) of the reactive dyes (B) of the formula (V), V is amino, W is hydroxy, h is 1, f is zero, g is 1,  $L^4$  is NHCO (where either the nitrogen or carbon atom thereof is attached to the group  $R^{14}$ ) and  $R^{52}$  is the group Het<sup>3</sup>, where Het<sup>3</sup> is a reactive group having an aliphatic chain. More preferably, in this range (v), the group Het<sup>3</sup> is a vinylsulphonyl group or  $SO_2CH_2CH_2Q^1$ , where  $Q^1$  is as defined above and still more preferably x is zero and  $R^1$  is a phenyl group substituted by a vinylsulphonyl group or

$\text{SO}_2\text{CH}_2\text{CH}_2\text{Q}^1$ , where  $\text{Q}^1$  is as defined above.

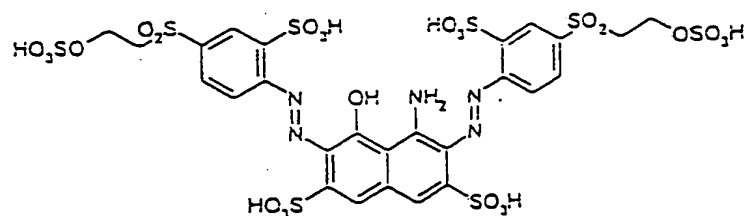
One especially preferred dye mixture contains a dye of the formula (105) as a dye of the formula (V)



and more preferably additionally contains a dye of the formula (44) as another dye (B), of the formula (II)

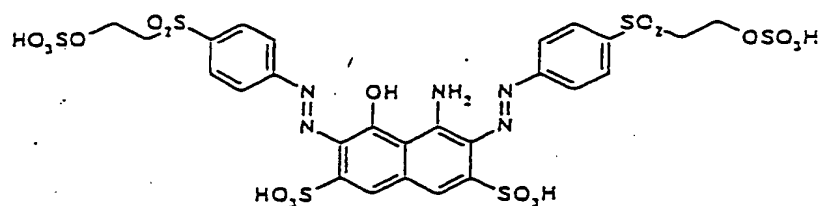


20 Another especially preferred dye mixture contains at least one and more preferably both of the dyes of the formulae (163) and (167)





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(167)

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Reference is now made to a dye mixture wherein the reactive dye (B) is a formazan dye of the formula (VI), given and defined above.

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In preferred respective ranges of the reactive dye (B) of the formula (VI)

(i) each of u and v is zero, i is 1,  $R^{16}$  is a sulphonic acid group or a salt thereof, j is 2 and one  $R^{17}$  is a sulphonic acid group or a salt thereof and the other  $R^{17}$  is a vinylsulphonyl group or  $SO_2CH_2CH_2Q^1$ , where  $Q^1$  is as defined above; and

25 (ii) v is zero, i is 1,  $R^{16}$  is a sulphonic acid group or a salt thereof, j is 1,  $R^{17}$  is a sulphonic acid group, u is 1 and Het<sup>1</sup> is a triazine ring substituted by a halogen

atom. In one preferred sub-range within the range (ii), each of k and l is zero, t is 1 and R<sup>61</sup> is a phenyl group substituted by at least one sulphonic acid group or a salt thereof, while in another preferred sub-range with the range (ii), each of k, l and t is 1, each of R<sup>60</sup> and R<sup>61</sup> independently is a phenyl group substituted by at least one sulphonic acid group or a salt thereof and Het<sup>2</sup> is a triazine ring substituted by a halogen atom. In yet another preferred sub-range within the range (ii), each of k and t is zero, l is 1 and Het<sup>2</sup> is a reactive group having an aliphatic chain.

Reference is now made to a dye mixture wherein the reactive dye (B) is a dye of the formula (VII), given and defined above.

In one preferred range of such dyes, x is zero and each of p, q, w and w<sub>2</sub> is 1. More preferably, in such a range, R<sup>1</sup> is a naphthalene ring substituted by at least one sulphonic acid group. It is also preferred that, in such a range, w<sub>3</sub> is 1 and R<sup>3</sup> is a methoxy group. Moreover, a preferred group of R<sup>20</sup> is hydrogen and preferred groups of R<sup>21</sup> are hydrogen, methyl and ethyl. A preferred group R<sup>4</sup> is a phenyl group substituted by at least one sulphonic acid group.

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In another preferred range of such dyes (VII), each of p, q, w<sub>1</sub> and w<sub>2</sub> is zero. More preferably, in such a range, w<sub>3</sub>

is 3 and at least one of  $R^3$  is a sulphonic acid group.

Other groups of  $R^3$  are preferably methyl, methoxy, amino or further sulphonic acid groups. It is also preferred that where, in such dyes,  $x$  is 1,  $R^1$  is a phenyl or naphthyl

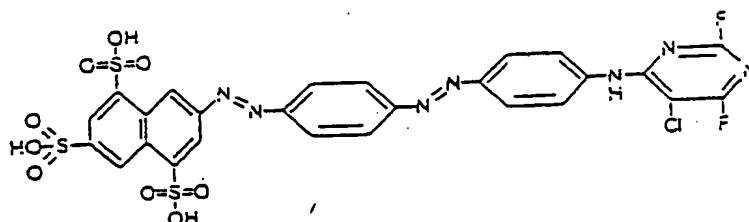
- 5 group substituted by at least one sulphonic acid group,  $L^1$  is NH and  $R^{40}$  is a reactive halopyrimidine group, especially a group containing at least one, more especially at least two fluorine atoms and particularly a difluorochloropyrimidine group, and that where, in such
- 10 dyes  $x$  is zero,  $R^1$  is a phenyl group substituted by a vinyl sulphonyl group or  $SO_2CH_2CH_2Q^1$ , where  $Q^1$  is as defined above and optionally additionally substituted by at least one methoxy group.

- 15 Reference is now made to a dye mixture wherein the reactive dye (B) is a disazo dye of the formula (VIII), given and defined above.

In one preferred range of such dyes,

- 20  $R^{55}$  is a naphthyl group;  
 $R^{56}$  is a sulphonic acid group or a salt thereof;  
 $R^{59}$  is a group  $L^{10}$ -Het, where  $L^{10}$  is the group N(H)- and Het is a reactive heterocyclic group substituted by at least one halogen atom;
- 25  $y_1$  is 1, 2 or 3; and  
each of  $y_2$ ,  $y_3$  and  $y_4$  is zero.

A particularly preferred such disazo dye of the formula (VIII) in a dye mixture embodying the invention has the formula



(71)

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In another preferred range of such dyes of the formula (VIII)

$R^{55}$  is a phenyl group;

the group  $R^{56}$  or each group  $R^{56}$  independently is a  
 15 sulphonic acid group or a salt thereof or is a reactive group selected from a vinyl sulphonyl group and a group  $SO_2CH_2CH_2Q^2$  in which  $Q^2$  is as defined above;

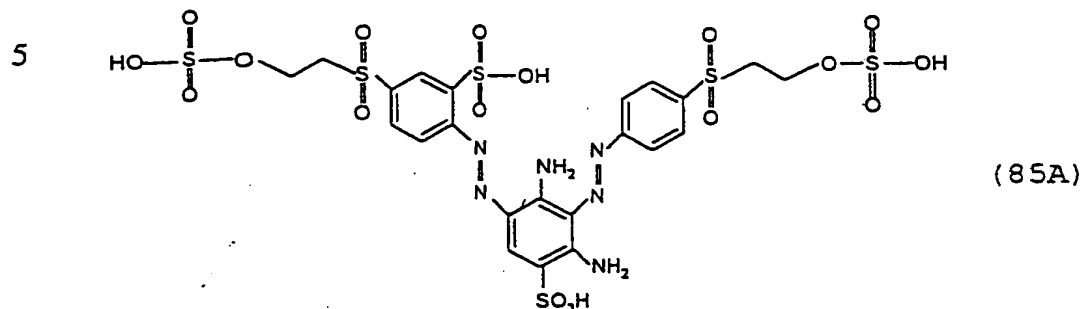
$y_1$  is 1 or 2; and

at least one group  $R^{56}$  is a said reactive group or the  
 20 group  $R^{59}$  is or includes a reactive group.

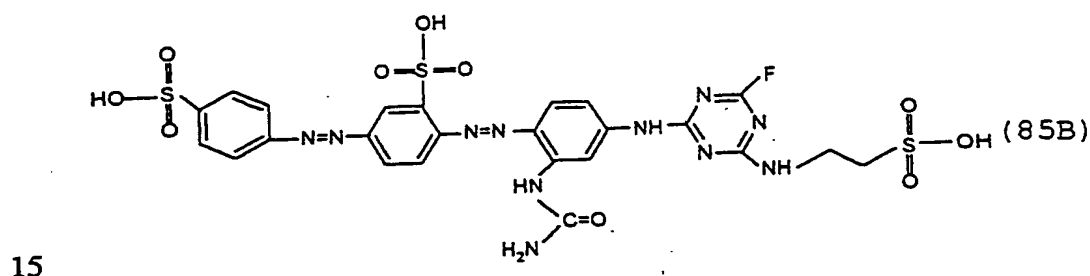
More preferably, at least one group  $R^{56}$  or the group  $R^{59}$  is a reactive group selected from a vinyl sulphonyl group and a group  $SO_2CH_2CH_2Q^2$  in which  $Q^2$  is as defined above; or  
 25 at least one group  $R^{56}$  is a sulphonic acid group or a salt thereof and  $R^{59}$  is the group  $L^{10}$ -Het, where  $L^{10}$  is the group N(H)- and Het is a reactive triazine group substituted by a

halogen atom and additionally by the group  $\text{NHCH}_2\text{CH}_2\text{SO}_3\text{H}$ .

Especially preferred dyes have the formulae



10 and



Reference is now made to a dye mixture wherein the reactive dye (B) is a phthalocyanine dye of the formula (X), given and defined above.

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Preferably, in the reactive dye (B) of the formula (X), respective average values of  $x_1$ ,  $x_2$  and  $x_3$  are  $x_1$  is 3,  $x_2$  is zero and  $x_3$  is 1, three of the four isoindole rings of the phthalocyanine have a respective sulphonic acid substituent (or a salt thereof) thereon and the other isoindole ring has a group  $\text{SO}_2\text{NH-B-NH-Het}$  substituted thereon. More preferably B is a straight or branched  $\text{C}_{2-4}$  alkylene group

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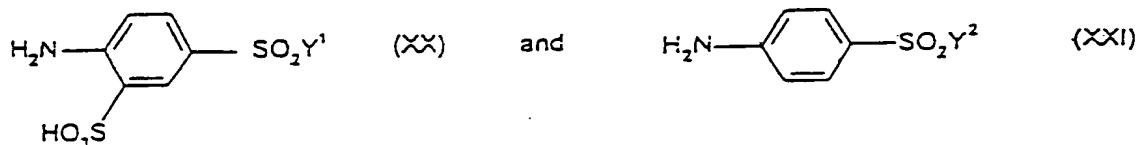
and Het is a triazine ring substituted by at least one halogen atom and optionally additionally substituted by a methoxy group.

- 5 Reference is now made to a dye mixture wherein the reactive dye (B) is a triphendioxazine dye of the formula (XI), given and defined above, or a salt thereof.

- 10 Preferably, in such a reactive dye (B) of the formula (XI), each of  $T^1$  and  $T^2$  is a halogen atom, each  $U^1$  is a sulphonic acid group or a salt thereof, each of  $B^1$  and  $B^2$  independently is a straight or branched  $C_{2-4}$  alkylene group, each of  $Het^1$  and  $Het^2$  independently is a triazine ring substituted by a halogen atom and each of  $R^{80}$  and  $R^{81}$
- 15 independently is a phenyl group substituted by at least one sulphonic acid group or a salt thereof.

The dyes of the formula (A) can be prepared by diazotising each of the amines (XX) and (XXI)

20



- wherein each of  $Y^1$  and  $Y^2$  is as defined above and firstly
- 25 coupling the diazotised amine (XXI) under strongly acid conditions (pH 1-2) to H-acid to provide an azo group ortho to the amine group and thereafter coupling the diazotised

amine (XX) under slightly acidic, neutral or alkaline conditions (pH 6-7) to the H-acid to provide an azo group ortho to the hydroxy group.

- 5 The diazotisation reactions may each be carried out by adjusting the pH of the amine with a buffer to about 5.3 - 6, adding an aqueous solution of hydrochloric acid and ice to cool to 0-5°C and then adding a sodium nitrite solution.
- 10 The coupling reactions may each be carried out by adjusting the pH as described above and allowing reaction to take place at a temperature of from 4 to 8°C for at least 3 hours.
- 15 These and other methods of preparing the dyes of the formula (A) are described in EP-A-0149170.

*Sub B1*

20 Likewise disazo dyes (B) of the formula (V) may be prepared in an analogous manner. Methods of preparation of such dyes are also disclosed in DE-A-3875658 and DE-A-3622080.

Dyes (B) of the formula (I) may be prepared by the methods disclosed in DE-A-3717667.

- 25 Dyes (B) of the formula (II) may be prepared by the method disclosed in DE-A-3927790, DE-A-3515651 and EP-A-0761768.

Dyes (B) of the formula (III) may be prepared by the methods disclosed in US-A-4618671, DE-A-3717814 and DE-A-

3829595.

Dyes (B) of the formula (IV) may be prepared by the method disclosed in US-A-4841031, EP-A-0343262 and EP-B-0776947.

5

Dyes (B) of the formula (VI) may be prepared by the methods disclosed in DE-A-3737536, DE-A-3743236 and DE-A-3840653.

10

Dyes (B) of the formula (X) may be prepared by the methods disclosed in WO-A-98/49240.

Dyes (B) of the formula (XI) may be prepared by the methods disclosed in DE-A-3423581 and EP-A-0773264.

15

Examples of dyes (B) of the formula (VII) are CI Reactive Yellow 57, CI Reactive Yellow 106, CI Reactive Yellow 160 and CI Reactive Yellow 167, all commercially available.

20

A preferred dye mixture in accordance with the invention comprises, by weight of the total weight of the dyes, from 10 - 99.5% by weight, inclusive of component (A), given and defined above, and from 0.5 to 90% by weight inclusive of component (B), given and defined above. Respective progressively more preferred ranges are as follows:

25

10 - 99% by weight, inclusive of component (A) and from 1 to 90% by weight, inclusive of component (B);



from 10 - 98.5% by weight, inclusive, of component (A) and  
from 1.5 - 90% by weight, inclusive, of component (B);

from 10 - 97% by weight, inclusive, of component (A) and  
5 from 3 - 90% by weight, inclusive, of component (B);

from 10 - 95% by weight, inclusive, of component (A) and  
from 5 - 90% by weight, inclusive, of component (B);

10 from 10 - 90% by weight, inclusive, of component (A) and  
from 10 - 90% by weight, inclusive, of component (B);

from 15 - 90% by weight, inclusive, of component (A) and  
from 10 - 85% by weight, inclusive, of component (B);

15 from 20 - 90% by weight, inclusive, of component (A) and  
from 10 - 80% by weight, inclusive, of component (B);

from 30 - 90% by weight, inclusive, of component (A) and  
20 from 10 - 70% by weight, inclusive, of component (B); and

In an especially preferred mixture, component (B) is a  
mixture of dyes (B).

25 Mixtures embodying the invention can be prepared by merely  
mixing the individual dyes or, in some cases, by synthesis  
using a mixture of diazotising components. This method is  
especially suitable when component (B) is at least one dye  
of the formula (V). The dye mixture may be isolated, for

example, by spray drying or salting out.

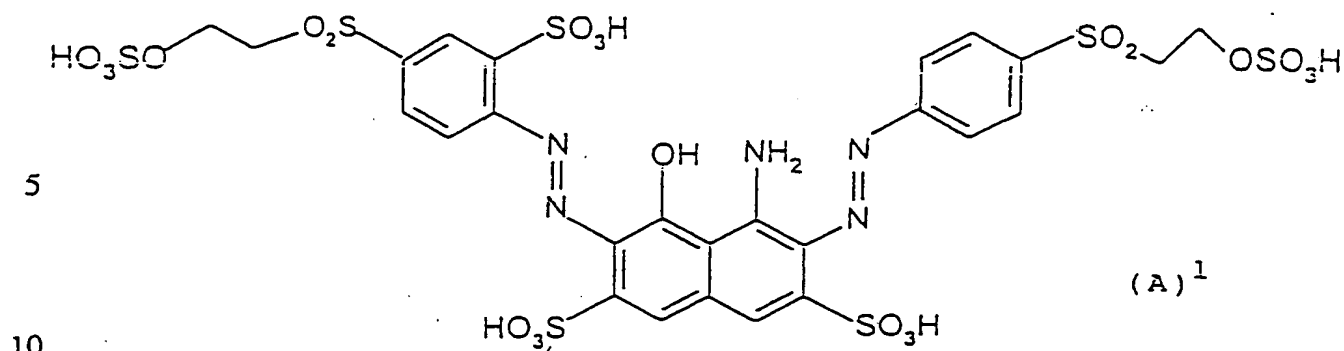
The mixtures can be used to dye or print on substrates containing a hydroxyl group or nitrogen atom, for example,  
5 silk, leather, wool, polyamides, polyurethanes and cellulosic materials, especially cotton.

The mixtures provide excellent properties including resistance to modern peroxide based detergents, fastness to  
10 repeat washing, good light fastness, excellent wash-off, good build-up, good compatibility of the dyes with one another and a robustness to process variables.

The reactive dye (A) alone gives a navy shade on cotton and  
15 may be mixed with at least one yellow, orange, red or blue reactive dye (B) to give a forest green, navy, brown or black shade.

The mixtures have outstanding properties in comparison with  
20 known mixtures, for example CI Reactive Black 5, referred to above, which is often used in a mixture with other dyes as a dulling agent.

Preferred embodiments of the invention will now be  
25 described in more detail with reference to the following Examples, in which the numbers assigned to the dyes are those given in Table 2 and all parts are by weight unless otherwise stated. In the Examples, dye A has the formula



Example 1:

15 75 parts of dye (A)<sup>1</sup>, 20 parts of dye (167) and 5 parts of dye (163) were mixed. The mixture was used to dye cotton, by application of cold pad batch and warm exhaust (40, 50 or 60°C) techniques as described below, in a navy shade resulting in good light fastness and fastness to repeated washing.

20 Exhaust application:

100g of cotton fabric were dyed in a dyebath that contained 1000 ml water, 12g of the mixture of Example 1, 2.5g sodium carbonate, 1g 32 weight% sodium hydroxide solution and 60g sodium sulphate decahydrate. The dyeing was started at 30°C, the temperature was raised to 50°C over a period of 30 minutes and the dyeing was continued for a further 60 minutes at this temperature. After cooling to room temperature the dyeing was

25

30 rinsed and boiled with detergent, and dried.

Cold pad-batch application:

At room temperature woven cotton fabric was soaked in a padder with dye liquor that contained per 1000g dye liquor 60g of dye mixture of Example 1, 50g sodium silicate (38° B'e) and 30g 32 weight% sodium hydroxide solution.

- 5 After 70% pick-up the paddings are rolled and covered with cling film. After storing for 8h at room temperature the paddings are removed from the cling film, rinsed in cold water, hot rinsed with detergent, and dried.

10 Example 2:

- 60 parts of dye (A)<sup>1</sup>, 24 parts of dye (44) and 16 parts of dye (105) were mixed mechanically. The dye mixture was applied to cotton using the application and fixing methods of Example 1, resulting in a black shade providing outstanding fastness properties.

Example 3:

- 20 Dye (A)<sup>1</sup> and dye (53) were synthesised separately according to known procedures. 65 parts of reaction solution of dye (A)<sup>1</sup> and 35 parts of reaction solution of dye (53) were mixed and the dye mixture was isolated by spray drying. The dye mixture was applied to cotton using the application and fixing methods of Example 1, resulting in a black shade providing outstanding fastness properties.

Further examples were made achieving the same outstanding fastness properties and these are given in Table 1:

Table 1

Example	Parts dye (A)	Yellow Dye No.	Parts Yellow Dye	Red Dye No.	Parts Red dye
4	60	10	20	126	20
5	58	14	25	127	17
6	65	23	14	121	21
7	55	44	25	129	20
8	70	49	15	91	15
9	65	15	10	105	25

Example	Parts dye (A)	Orange Dye No.	Parts Orange dye
10	67	55	33
11	62	61	38
12	60	69	40

Still further (binary mixture) examples were made and when applied via the cold pad-batch application method of Example 1 achieved the same outstanding fastness properties, as shown in Table 2.

Table 2

Example	Parts dye (A)	Yellow/Orange Dye No.	Parts Yellow/Orange dye
10	15	17	10
	16	34	10
	17	17	49
	18	34	49
	19	17	44
15	20	34	44
	21	17	23
	22	34	23
	23	17	61
	24	34	61
20	25	17	53
	26	34	53
	27	17	67
	28	34	67
	29	17	85A
25	30	34	85A
	31	17	85B
	32	34	85B

Example 13:

100g of cotton fabric was dyed according to the procedures  
5 described for Example 1 using 3g of a dye mixture  
containing 1.5g dye (A)<sup>1</sup>, 0.6g dye (1), 0.3g dye (2) and  
0.57g dye (94) resulting in a brown shade providing  
outstanding fastness properties.

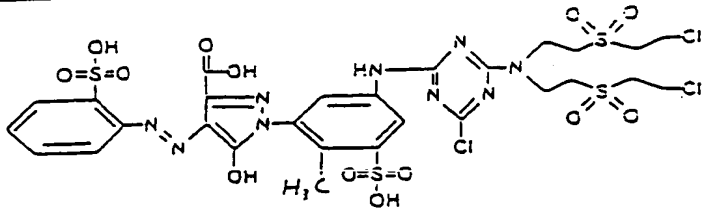
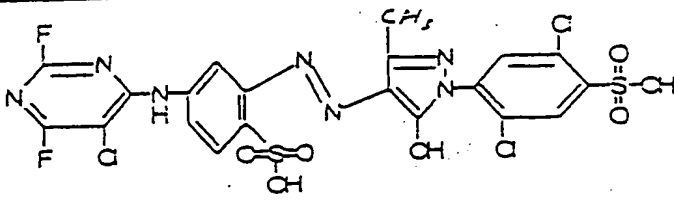
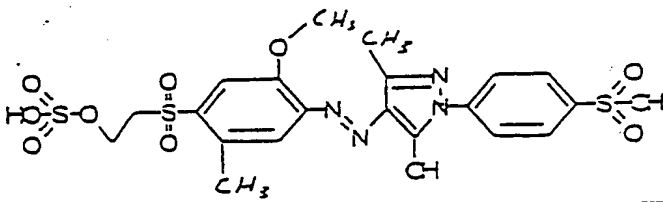
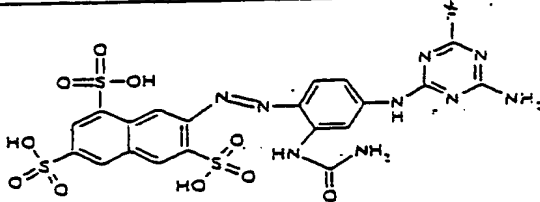
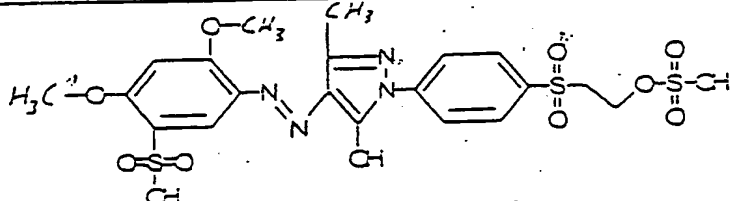
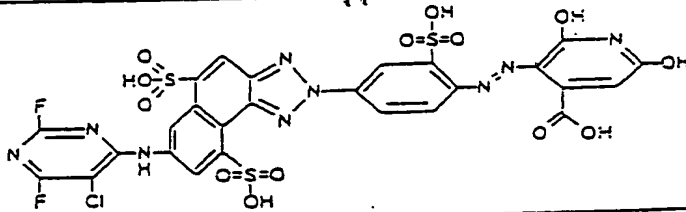
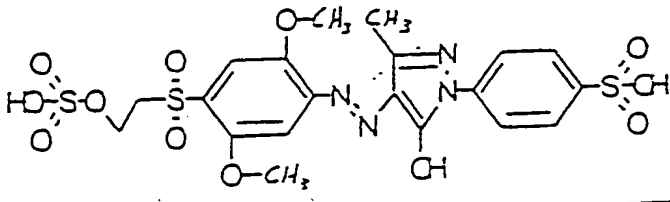
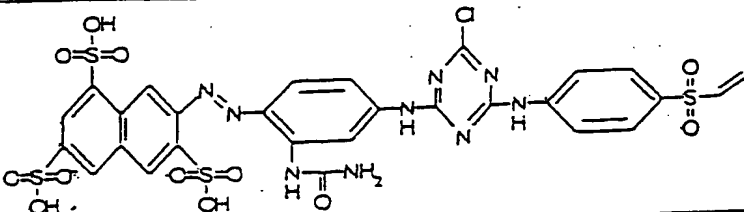
10 Example 14:

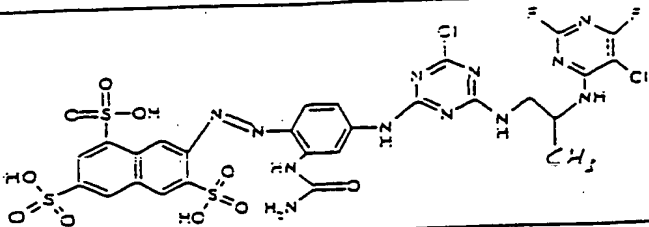
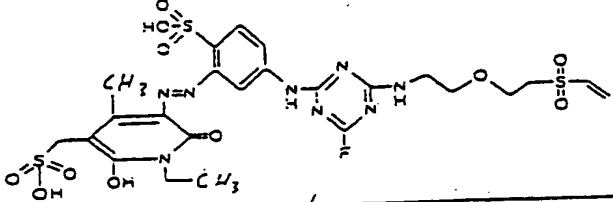
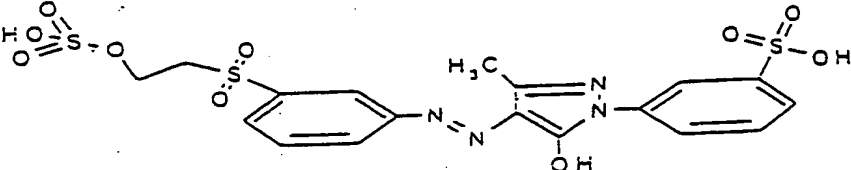
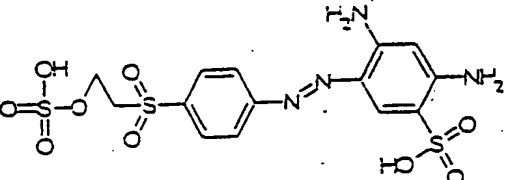
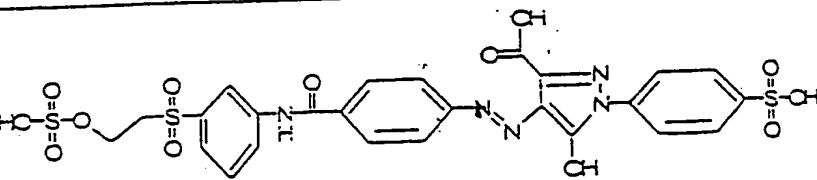
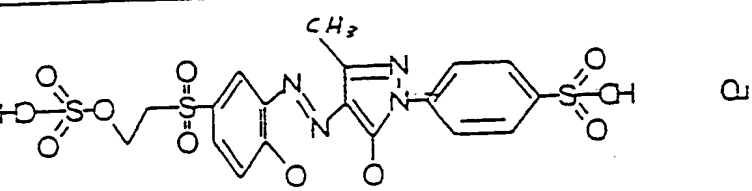
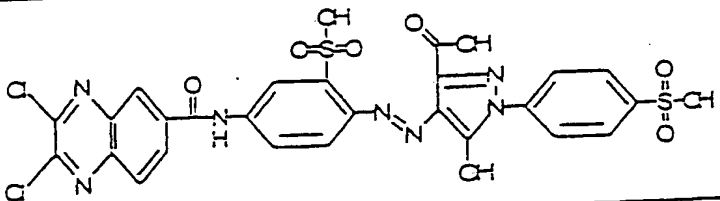
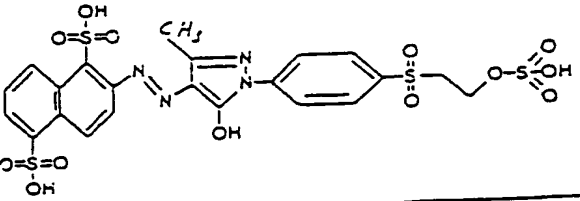
100g of cotton fabric was dyed in a dyebath that contained  
1000ml water, 3g of a mixture containing 1.4g dye (A)<sup>1</sup>,  
0.13g dye (150), 0.54g dye (15), 0.30g dye (69), 0.28g dye  
15 (90) and 0.35g dye (101), 15g sodium carbonate and 60g  
sodium chloride. Dyeing was started at 40°C, the  
temperature was raised to 60°C over a period of 20 minutes  
and dyeing was continued for a further 60 minutes at this  
temperature. After cooling to room temperature the dyeing  
20 was rinsed and boiled with detergent resulting in a brown  
shade providing outstanding fastness properties.

For each of the dyes shown in Table 2 below, dye mixtures  
may be applied according to any of the procedures described  
25 in Examples 1 and 14 or by similar application methods to  
achieve outstanding fastness properties.

No.	Dyes	Colour on cotton
1		yellow
2		yellow
3		yellow
4		yellow
5		yellow
6		yellow
7		golden yellow



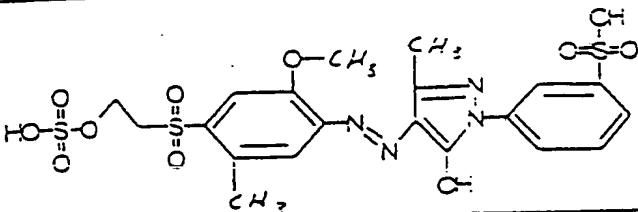
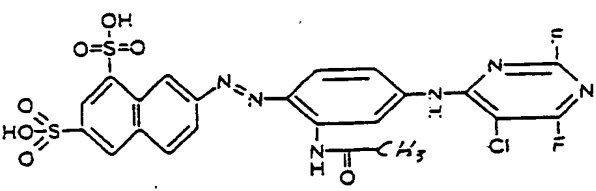
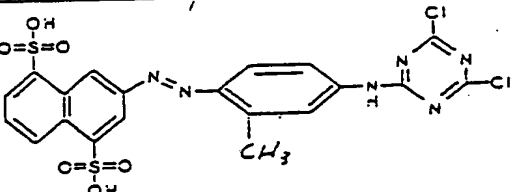
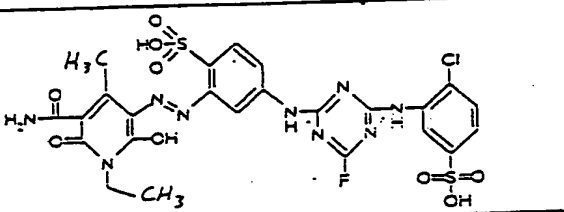
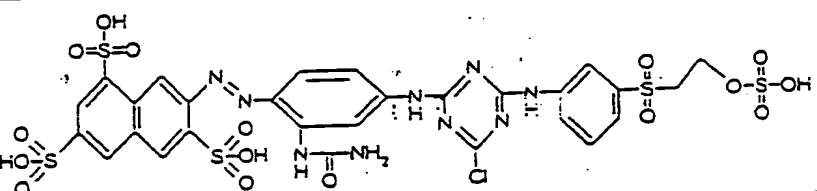
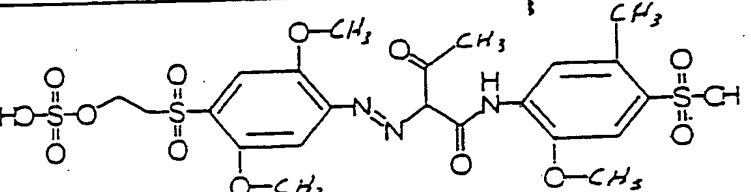
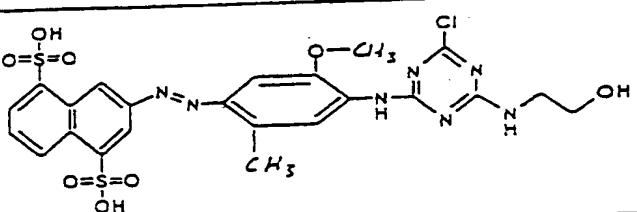
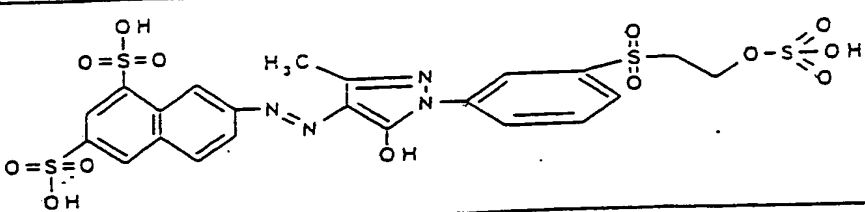
8		yellow
9		yellow
10		yellow
11		yellow
12		golden yellow
13		golden yellow
14		yellow
15		yellow

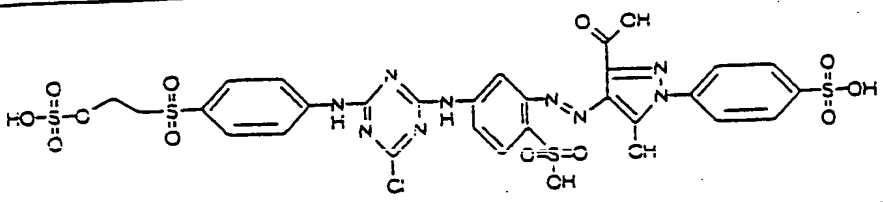
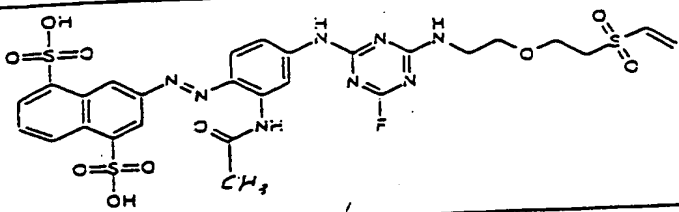
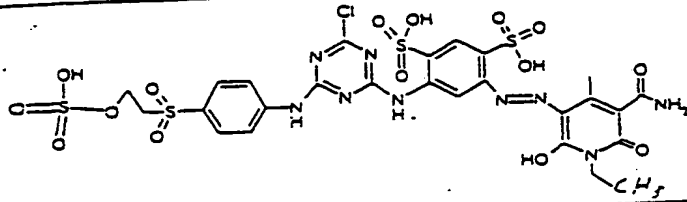
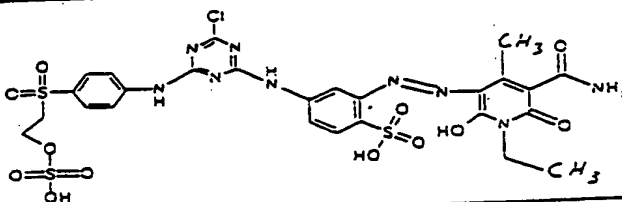
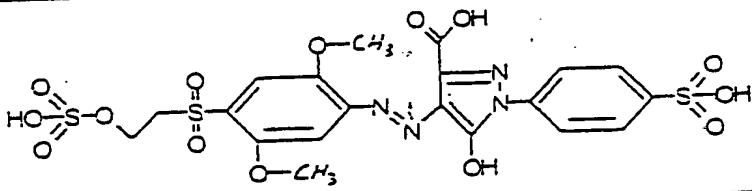
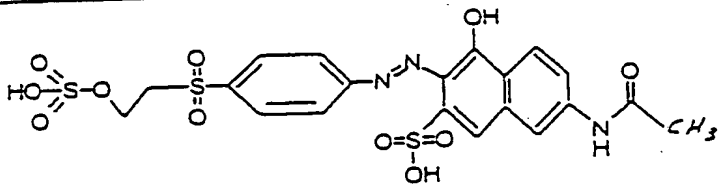
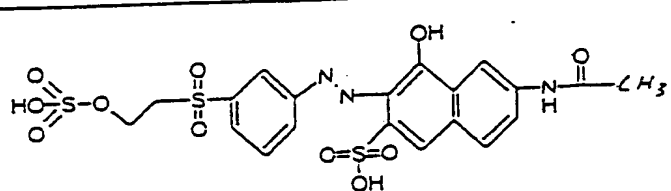
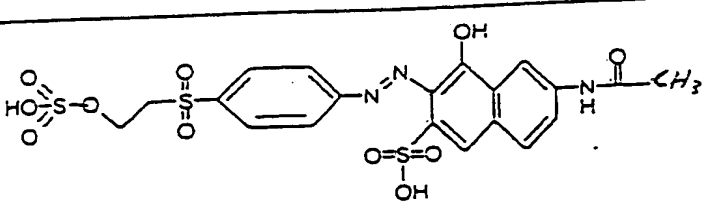
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18		yellow
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20		yellow
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22		golden yellow
23		yellow

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25		yellow
26		yellow
27		yellow
28		yellow
29		golden yellow
30		yellow
31		golden yellow

51

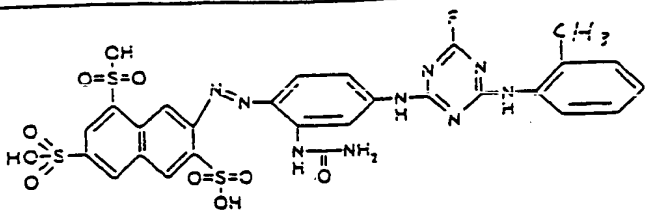
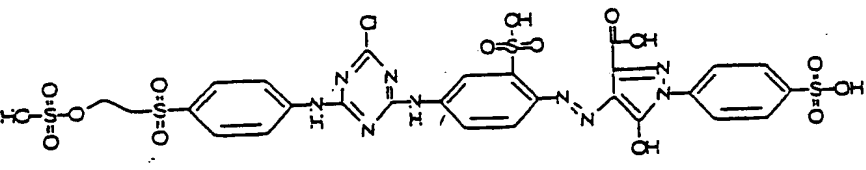
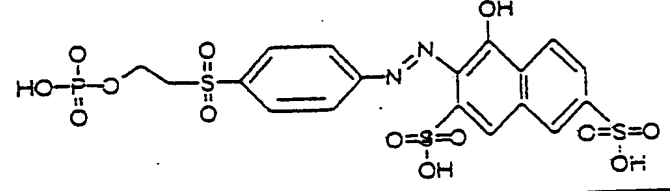
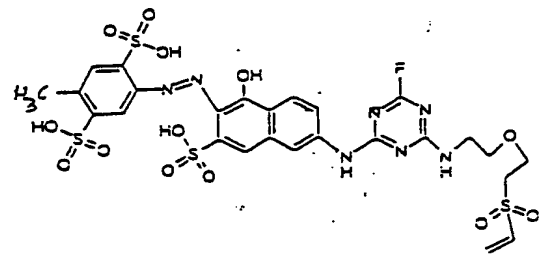
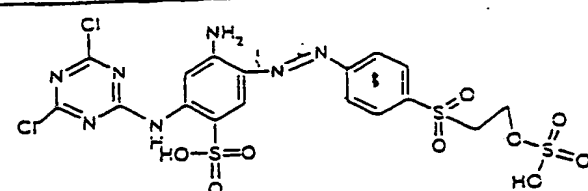
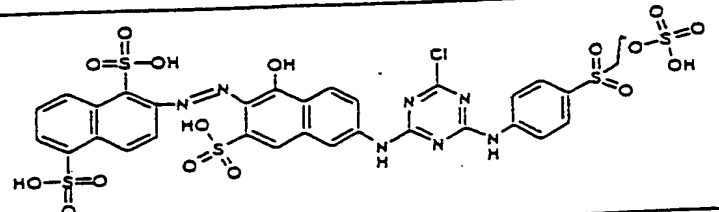
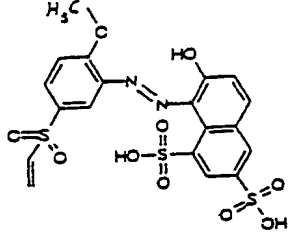
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35		yellow
36		yellow
37		yellow
38		yellow
39		yellow

40		yellow
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43		yellow
44		yellow
45		yellow
46		golden yellow
47		yellow

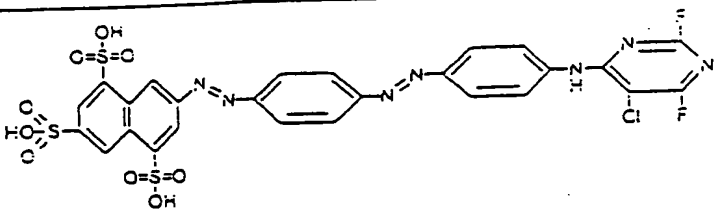
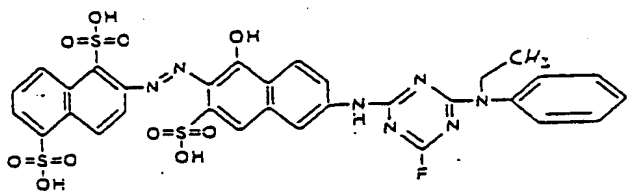
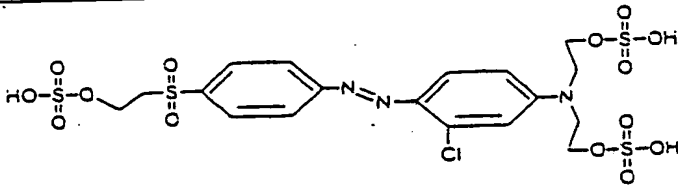
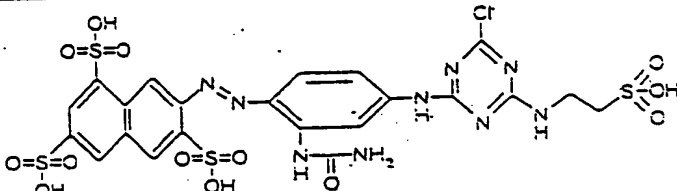
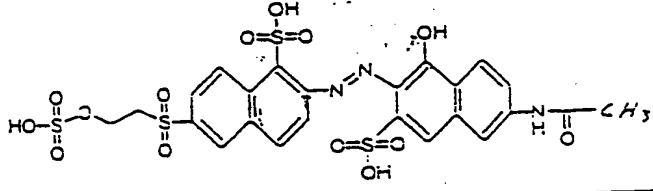
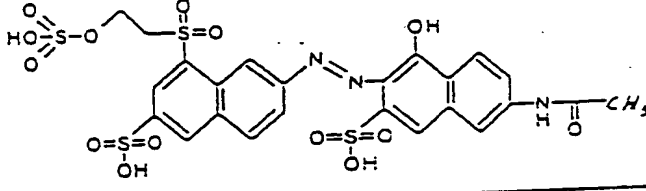
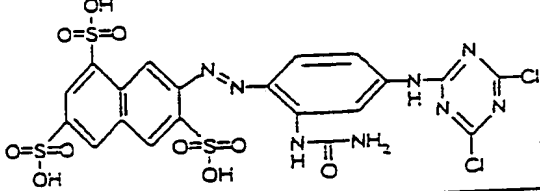
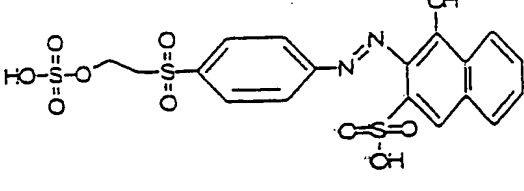
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53		orange
54		orange
55		orange

56		orange
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58		orange
59		orange
60		orange
61		orange
62		orange
63		orange

55

64		orange
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66		orange
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69		orange
70		orange

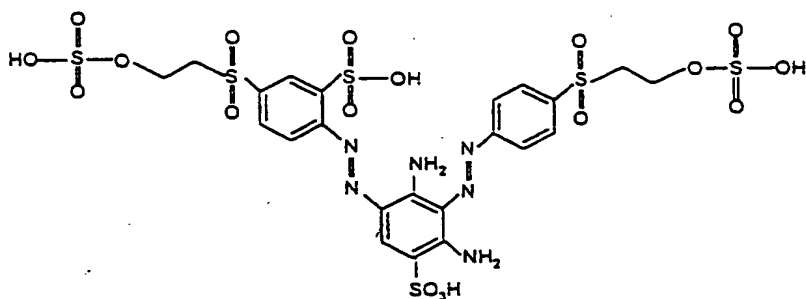


71		orange
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73		orange
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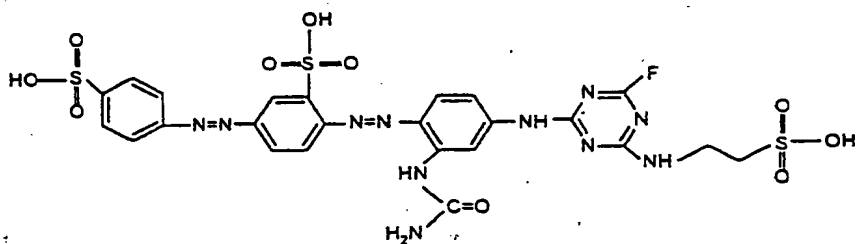
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85A



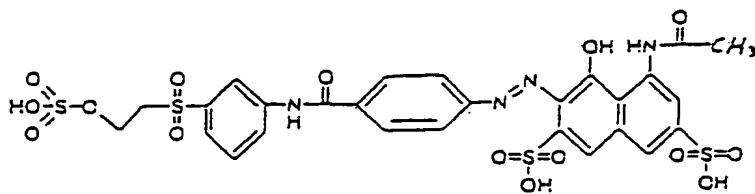
ORANGE

85B



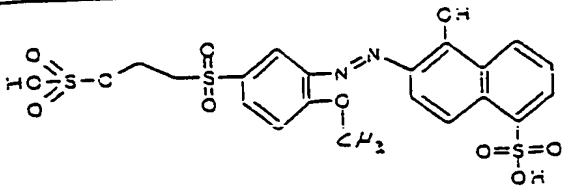
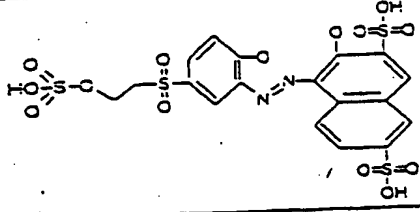
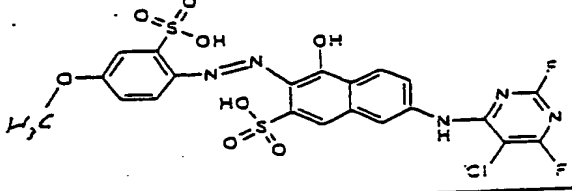
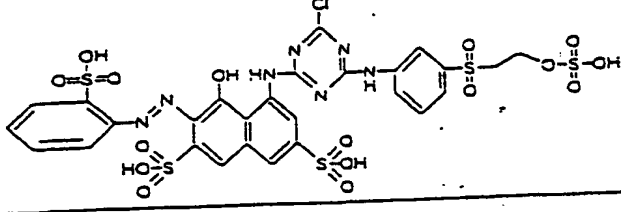
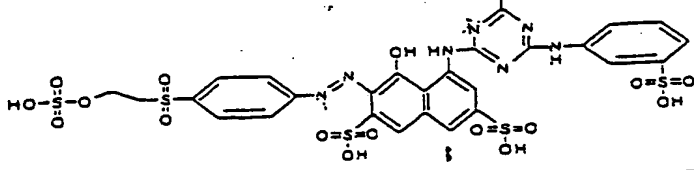
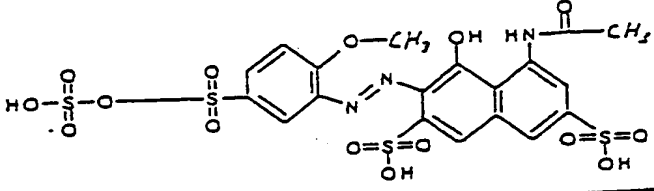
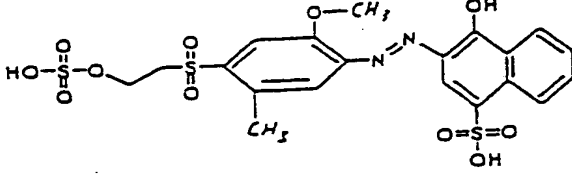
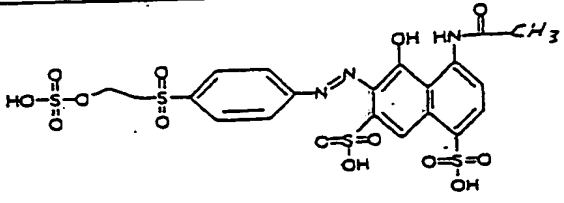
ORANGE

86



red

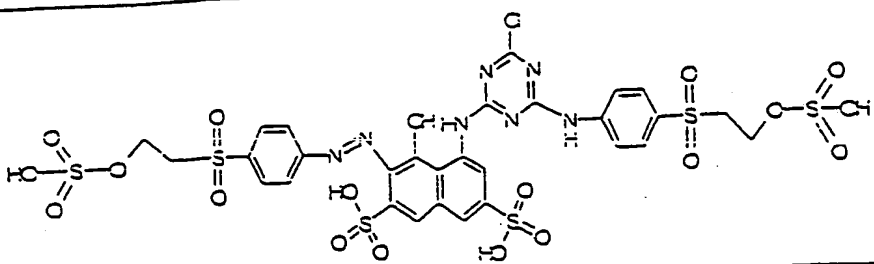
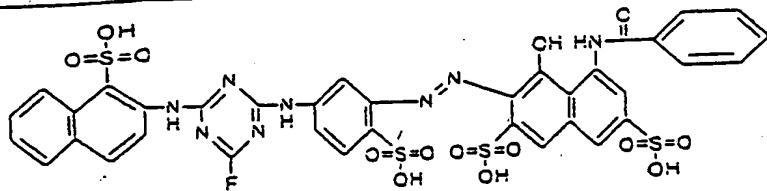
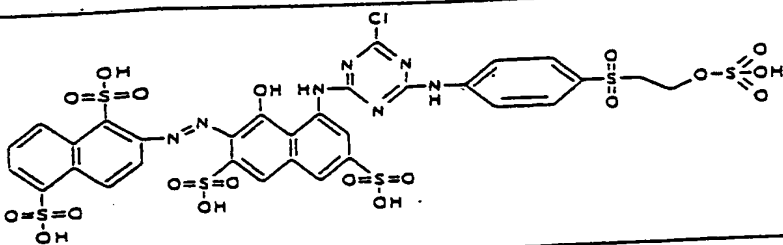
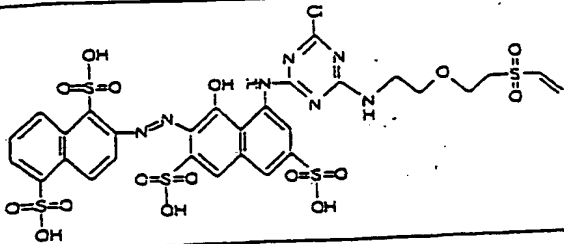
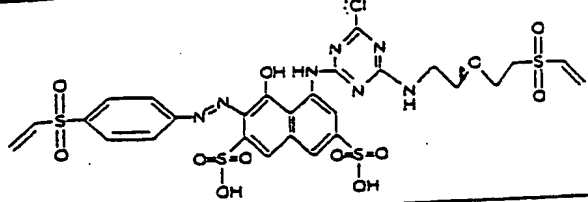
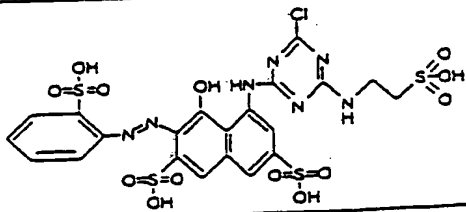
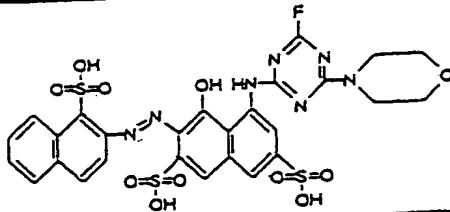
59

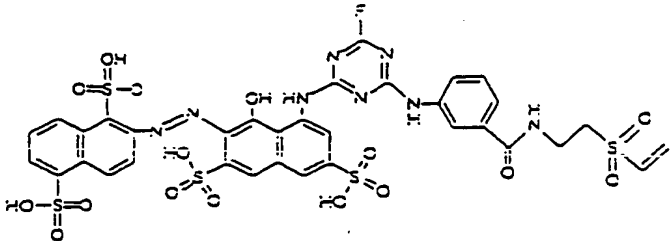
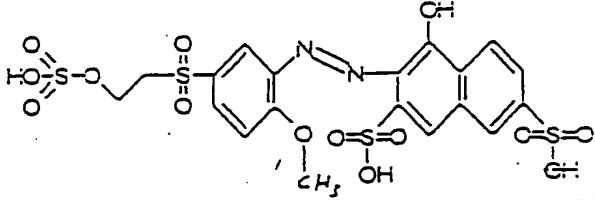
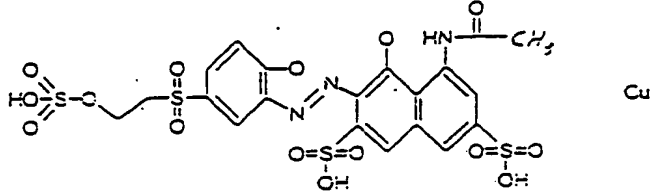
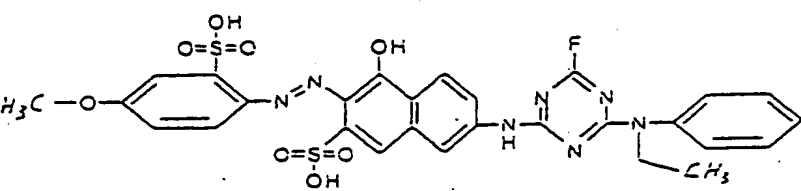
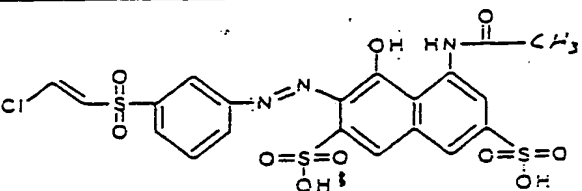
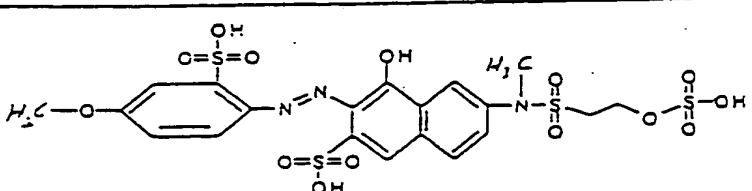
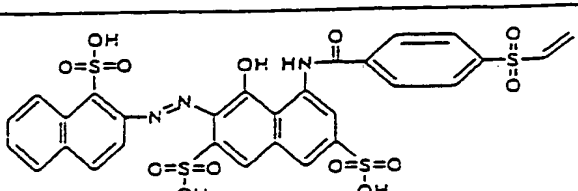
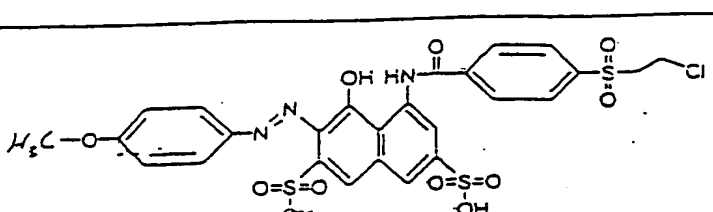
87		red
88		red
89		red
90		red
91		red
92		red
93		red
94		red

60

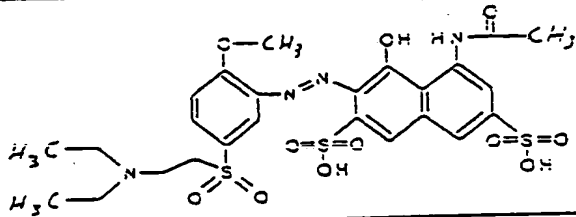
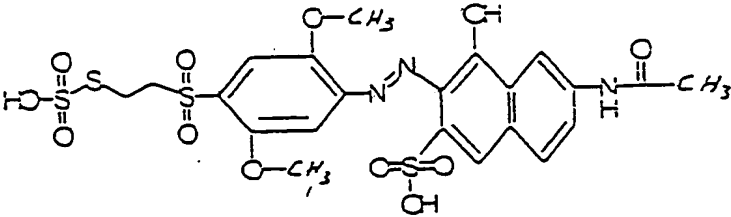
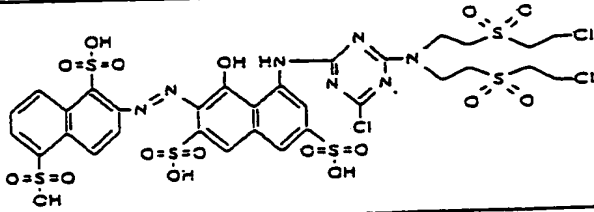
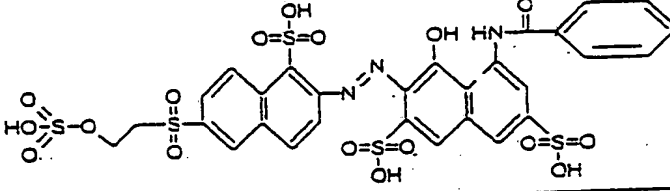
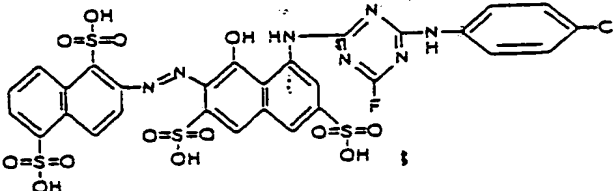
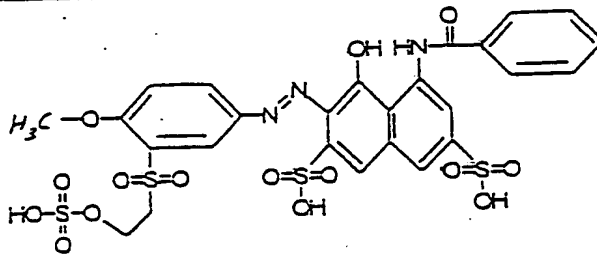
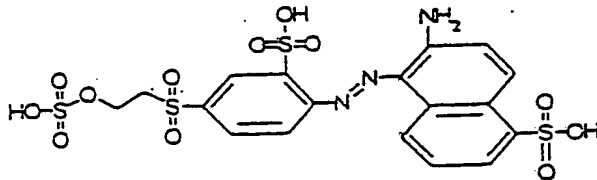
95		red
96		red
97		red
98		red
99		red
100		red
101		red
102		red

61

103		red
104		red
105		red
106		red
107		red
108		red
109		red

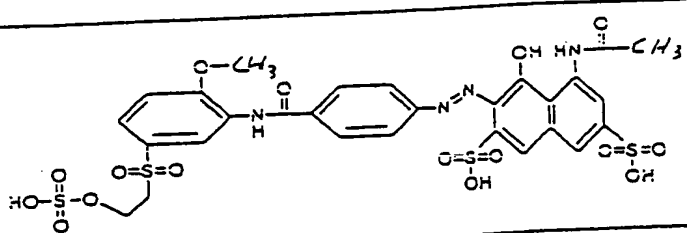
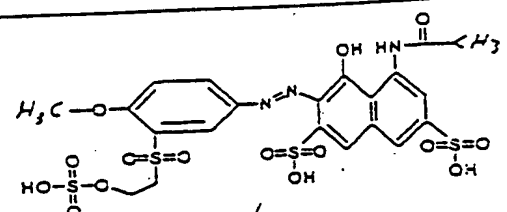
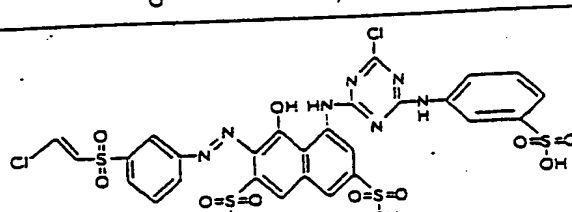
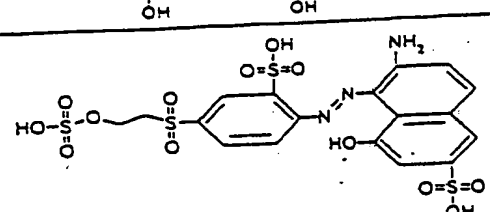
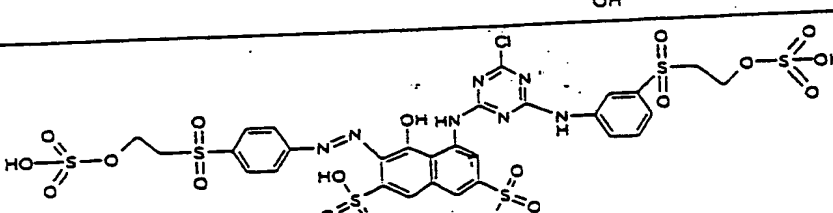
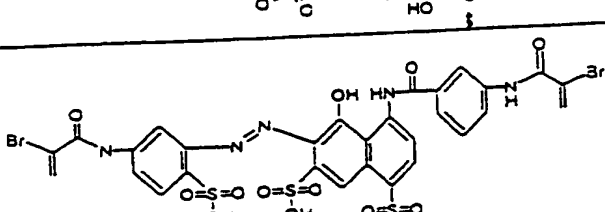
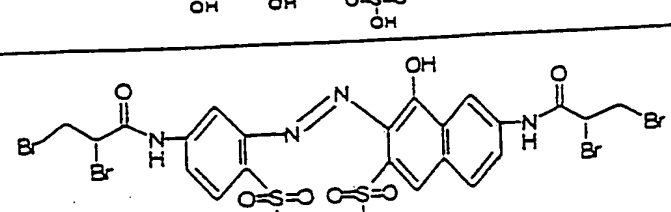
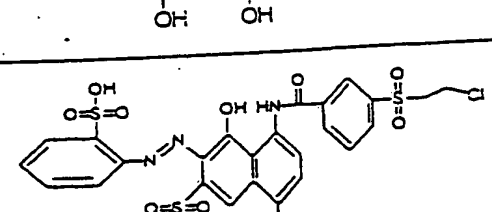
110		red
111		red
112		bluish red
113		red
114		red
115		red
116		red
117		red

63

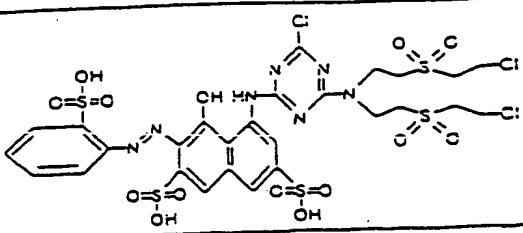
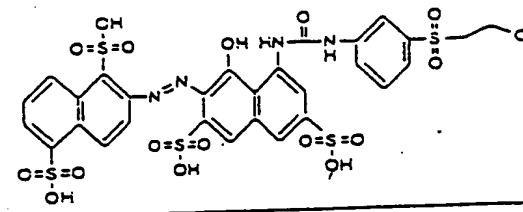
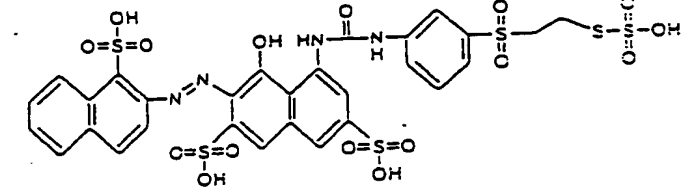
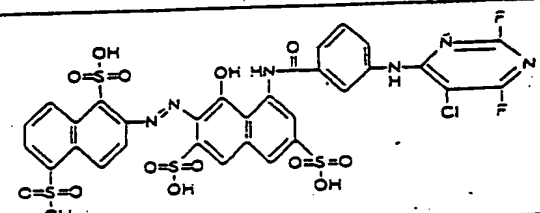
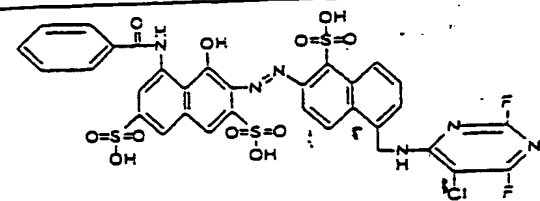
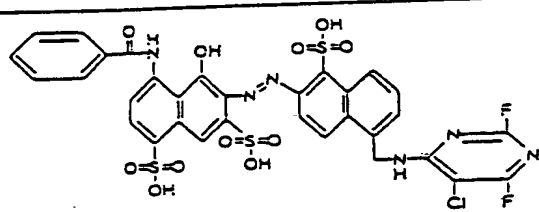
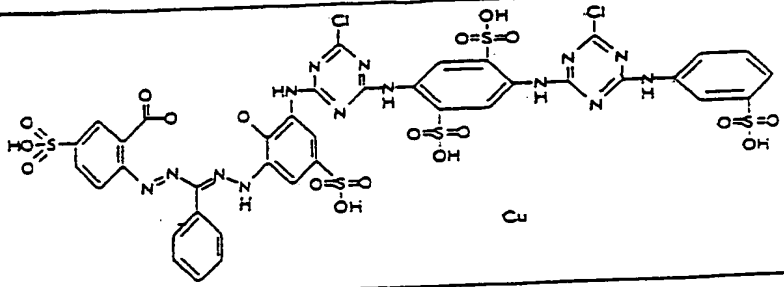
118		red
119		red
120		red
121		red
122		red
123		red
124		red



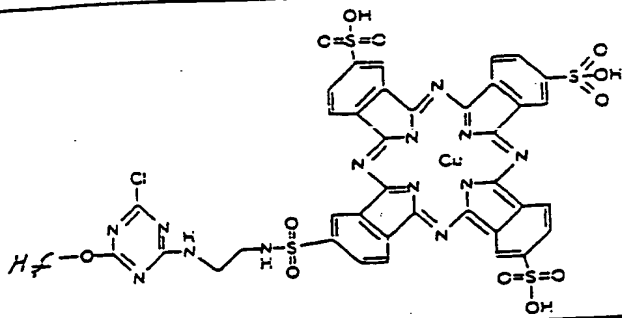
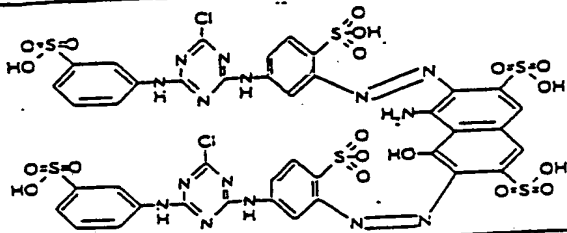
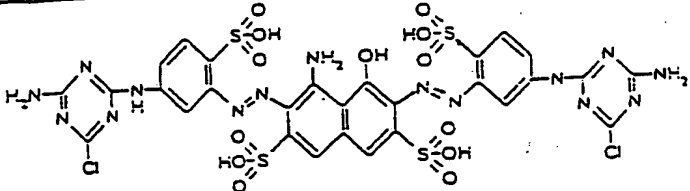
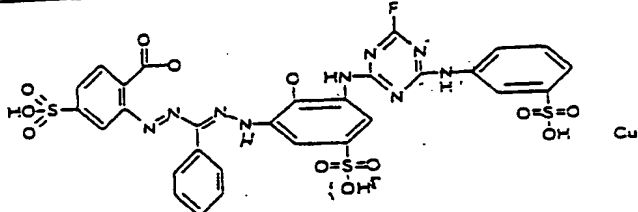
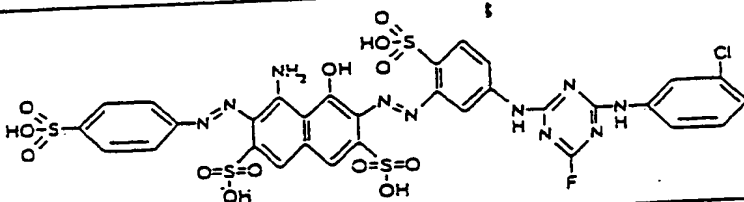
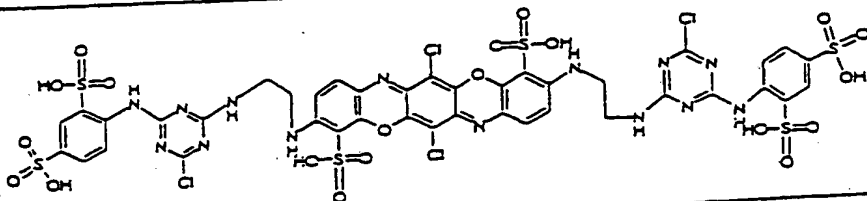
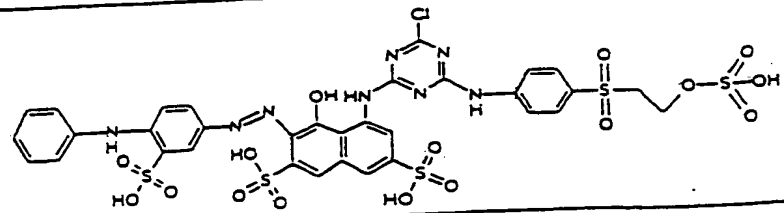
No.	Dyes	Colour on cotton
125		red
126		red
127		red
128		red
129		red
130		red
131		red

132		red
133		red
134		red
135		red
136		red
137		red
138		red
139		red

66

140		red
141		red
142		red
143		red
144		red
145		red
146		blue

67

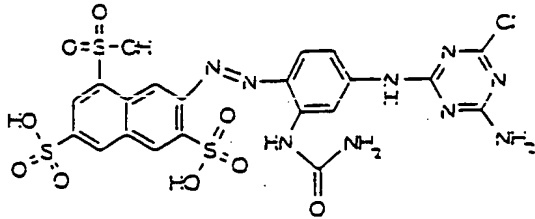
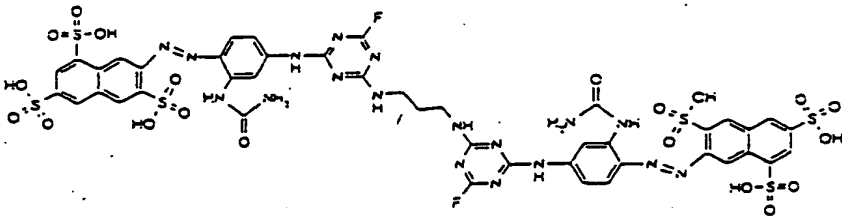
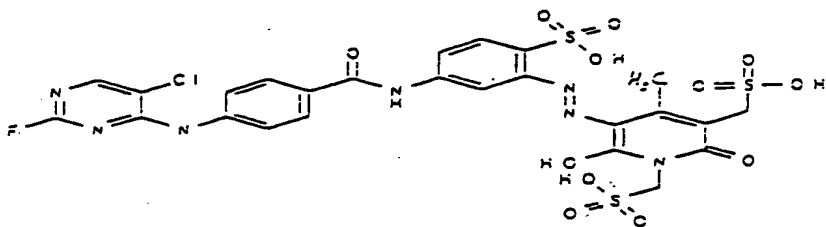
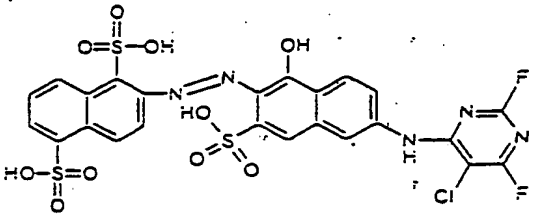
147		turquoise
148		navy
149		navy
150		blue
151		navy
152		blue
153		blue

68

154		navy
155		navy
156		navy
157		blue
158		navy
159		navy
160		blue

161		navy
162		navy
163		navy
164		navy
165		navy
166		navy
167		navy

70

168		orange
169		yellow
170		yellow
171		orange